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AND THE NECESSARY MECHANICAL EQUIPMENT

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CONTENTS OF THIS ISSUE

Contents of previous issues can be found by consulting the Industrial Arts Index at your library

General Index

Some Recent Developments in Waterproofing..... 167
By C. H. S. Tupholme
Technical Notes from Foreign Sources..... 170
New Products and Trade Notes..... 197

Index to Proceedings of American Association of Textile Chemists and Colorists

Standard Wash Fastness Samples..... P173
Problems Involved in Finishing Heavy-Weight Silk and Rayon Fabrics..... P174
A paper by Dwight L. Johnson
The Oxidation of Wool: The Effect of Hydrogen Peroxide..... P180
By Arthur Smith and Milton Harris
The Oxidation of Wool: The Lead Acetate Test for Hydrogen Peroxide-Bleached Wool..... P183
By Arthur Smith and Milton Harris
Calendar of Coming Events..... P185
Mercerizing Committee Meeting..... P185
A Test for Mercerization in the Presence of Dyes.. P186
By Sidney M. Edelstein
Applicants for Membership..... P190
Stainless Steel in the Textile Industry..... P191
A paper by George W. Hinkle

Editorial:

Wet Processing and the Knitting Arts Exhibition..... 193

Official Publication of the American Association of Textile Chemists and Colorists

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"To encourage in any practicable ways research work on chemical processes and materials of importance to the Textile Industry.

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VOLUME XXV APRIL 6, 1936 NUMBER 7

Some Recent Developments in

Waterproofing

By C. H. S. TUPHOLME

THERE are few fields in the textile industry more productive of interesting research or surprising results than that of waterproofing fabrics. Consider, for example, the announcement made on behalf of a German waterproofing concern of their (to use their own words) "surprising discovery that wool and other animal fibers are rendered to a high degree repellent to water in every stage of the working-up process by treatment with solutions of water-soluble soaps (i.e., water-soluble salts of fatty acids with at least 10 carbon atoms) provided this treatment is carried out after the goods have been thoroughly cleaned." It is an essential condition of this surprising effect that the surface of the fibers must be freed from impurities. The process, it is claimed, can be applied to loose wool, yarn, or fabric, for example, knitted or woven goods, whether in a raw, bleached or dyed condition. After treatment the goods are rinsed, preferably in cold water. It is stated that the effects produced by this process have in practice an unlimited resistance to the usual washing agents.

The usual textile soaps may be used in the treatment, such as shredded potash soaps, Marseilles soap, soap flakes and soap powder. The concentration of the solution may be varied, but to obtain good results not less than 0.5 gm. per liter and, for practical purposes, not more than 10 gm. per liter are used. It is usual to use 1-4 gm. per liter. The operating temperature is, for choice, held between 25 and 30° C. though in the case of thicker materials it may be an advantage to raise it to 45-50° C.

The duration of the process has a comparatively small influence when the temperatures are low. The water repellency appears to be produced almost instantaneously and it is immaterial whether the treatment lasts for 5 minutes, 10 minutes, 30 minutes or an hour. At higher temperatures the effect deteriorates if the treatment is prolonged. A quarter of an hour is, for instance, quite sufficient if the temperature is 50° C. The addition of sodium carbonate is always beneficial if there is any possibility of the material still containing traces of acid, but it may also be useful in other cases. Not more than 2 gm. per liter are used.

Where sufficient resistance to water is not obtained by a single treatment using this German process it is sometimes advisable to repeat it. The exact way in which the process is performed will depend to a large extent on the previous treatments to which the material has been subjected, and on whether impurities due to the pretreatment and only washed out with difficulty adhere to the fibers or not.

The process can most easily and successfully be applied to materials which have previously been dyed in the boiling liquor of an acid-dye bath. The dyeing process itself ensures a thorough cleaning of the fibers and if the cleaning is merely completed by very careful rinsing and neutralization the soaping produces the most favorable results without further difficulty. Greater attention is, however, necessary if the material has finally been fulled or carbonized. In such cases the ordinary rinsing is often insufficient to free the fiber from substances which are active on the surface. The preliminary washing is therefore done with particular care, by using soap in higher concentration and in a relatively small quantity of liquor, or by using synthetic washing agents or alumina. The preliminary washing is always accompanied by neutralization.

The quantity of liquor to be used in the actual proofing treatment must in no case be too small, so that the accumulation in the liquor of any impurities which may still be present does not attain too high a concentration. A quantity of liquor 10-20 times the weight of material is general. Where the goods have been dyed from an acid bath the volume of liquor may be reduced to, say, 5-10 times the weight of material.

As the effect is destroyed by acid the process must always follow the last acid treatment. Fulling and bleaching should also preferably precede it. Finishing processes carried out by mechanical means or by steam may, however, follow it.

Another process, which employs aluminum dust, emanates from France. This powder has, it is claimed, when incorporated in a plastic material, the property of giving a product that is much more elastic than the initial one. Aluminum is attacked with difficulty by oxidation and is without action on fatty bodies. Tests have shown that varnishes which are dried by oxidation have their polymerization influenced by the aluminum and that the final transformation product is always more elastic than the same product which dries without aluminum. Finally, aluminum has, in view of all its properties, to be considered as an excellent insulator of calorific radiation.

It is owing to the observation of these different properties that the originator of this idea proposes to waterproof fabrics with the aid of aluminum dust. His process is intended to form a really waterproof coating which can be conveniently applied and which penetrates deeply into the fabrics which it covers.

The fabrics to be made waterproof are impregnated with aluminum dust in a solution of paraffin wax containing a plasticizing agent. Normally, the solvent used for the paraffin wax is heavy benzine, the boiling point of which is about 160° C., and preferably the proportion of the aluminum dust in the solution is between 5 and 20 per cent. A suitable plasticizing agent consists of para rubber.

No further details of this process are available, but the inventor claims for it the following advantages:—

1. Great suppleness of the coating and considerable elasticity.
2. Great conservation of the waterproofing properties and of the suppleness of the fabric.
3. Fabrics so treated become very bad media for transmitting calorific radiations.
4. The waterproofing is increased by reason of the introduction into the waterproofing mass of an inert material which blocks up the pores, thus acting on the whole like a caulking.
5. The external appearance of the cloth is improved in a lasting manner, owing to the inert character of aluminum.

A third process involves the impregnation of unwoven textiles with vulcanized rubber latex. This process consists in forcing into the material under fluid pressure an aqueous dispersion of vulcanized rubber latex. In one form of the process the textile material is subjected to more than one treatment with vulcanized rubber latex and between successive treatments the textile material is removed and subjected to a vacuum. Alternatively, the material may be subjected to a vacuum immediately before the first and after the last treatment with the vulcanized latex. In a modified form of the process, the textile material is immersed in vulcanized latex in a closed vessel, and vacuum and pressure are applied alternatively, with or without its removal from the vessel.

The viscosity of the vulcanized rubber latex and the fluid pressure applied may be so adjusted that the latex is forced between and completely surrounds the individual fibers of the textile threads.

Another modification of the process consists in impregnating the material with an unvulcanized rubber dispersion prior to the treatment with vulcanized rubber latex. The unvulcanized dispersion may be coagulated and vulcanized prior to subjecting the material to impregnation treatment with the vulcanized rubber latex. The vulcanized latex may be introduced in two or more stages, and the properties of the successive latex baths may be varied so as to obtain, in successive layers, rubber differing in properties. Under certain conditions of impregnation it may be desirable to guard against any tendency to premature coagulation of the vulcanized latex and to increase the ease of impregnation. When this is the case any of the well-known stabilizing and wetting agents, such as casein, glue, soaps, sulfonated alcohols, etc., may be added.

The impregnating mix is made up as follows:— To latex of 60 per cent concentration, taking a quantity corresponding to 100 gm. dry rubber content, is added a paste consisting of 4 gm. sulfur, 0.5 gm. zinc oxide, 0.5 gm. of piperidine pentamethylene dithiocarbonate, the paste being prepared by adding to the solids 11 c.c. of a 2 per cent solution of saprotin and 2.5 c.c. of a 5 per cent casein solution. To the latex mixture thus prepared are added 2.7 c.c. of a 50 per cent solution of a stabilizing and wetting out agent, 2.7 c.c. of a 10 per cent solution of sulfonated lorol and 2.7 c.c. of a 10 per cent saprotin solution. These three substances are mixed together before adding to the latex mixture. Finally, water to reduce the combined mixing to 48 per cent dry rubber content is added. The dilute latex mixture is then vulcanized by raising the temperature during 1 hour gradually to 75° C. and then keeping it, stirring occasionally, for 1 hour at this temperature. After cooling and allowing the solids to deposit by standing, the mixture is strained.

The impregnating mix is used in the treatment of cotton yarns as follows: Cotton yarn is wound on bobbins and is then treated with the vulcanized latex after being subjected to a preliminary kier boiling and treatment with any of the well known wetting agents, which assists the subsequent impregnation with the vulcanized latex.

The impregnation is carried out by subjecting the bobbins in the closed vessel to a vacuum of 28 in. mercury, then introducing the vulcanized rubber latex mix into the closed vessel so as to cover the bobbins and subjecting the latex to a pressure of 100 lb. per sq. in. for 15 minutes. The latex is then withdrawn and vacuum again applied and this sequence of operations is repeated twice. The bobbins are then subjected to vacuum to remove excess of vulcanized latex and are removed from the vessel to be subjected to a maturing process. The yarn is subsequently wound off through a coagulating bath of dilute acetic acid and is then dried and rewound.

Controversy over the one-bath versus the two-bath method of waterproofing rayon still rages in Europe, but opinion is definitely crystallizing in favor of the former.

A notable protagonist of the one-bath process is H. Schonefeld who claims in an article published in *Melliand Textilberichte* that the modern one-bath process imparts a pleasant handle together with the water-repellent effect required, and gives great scope for individual treatment in finishing. The old alumina-soap method is said to be inferior because it has been found impossible to avoid the decomposition of aluminum salts on rayon materials without a very high degree of practical skill and experience. In any case the typical alumina handle must result, and is disliked by all.

Even with very careful handling the surface of the goods easily becomes smudged by lime soap precipitates. Moreover, superfluous alumina soap in the treatment baths plasters up the material with deposits which are hard to remove. Black materials suffer particularly in finishing. To obtain the desired proofing effect it is sometimes necessary to repeat the process, with intermediate dryings, several times so that it would be more correct to speak of a multi-bath than of a two-bath process. It is also difficult to avoid tendering due to the saturation of the rayon with various chemicals.

Improvements in the modern one-bath method, with assistants, give better results, according to Schonefeld. The waterproofing itself, owing to the substantivity of most of the media for one-bath work, is extremely level and intensive and gets right into the heart of the yarn. Each thread is separately enveloped with a thin yet dense film which results in perfect water resistance.

The original luster of rayon, which can hardly be retained with the use of alumina salts, remains untouched by good one-bath waterproofing assistants and can be even improved by very heavy calendering. The chemical and colloid-chemical properties of good one-bath proofing media guarantee a better drip-off effect (balling of drops of water as opposed to soaking in) than with any two-bath method. Highly dispersed proofing media remain stable in long standing baths and allow cheap treatment by continuous flow baths.

Waterproofers, like all other operators in the textile trades, have their troubles, many of them due to processes which have preceded the actual waterproofing operation. Some of these troubles, due to fabric damage, were recently reviewed in a lecture by Dr. Percy Bean, M.Sc. In the first place, Dr. Bean pointed out, a cloth might be unsuitable for proofing with a particular proofing because of its structure or quality. One good example was a pattern woven from two beams at different tensions. Another instance was a batch of proofings on a low quality fleece cloth in which the irregularities were so great that they showed through the rubber and spoiled the fabric for its purpose.

With regard to cloth treatment, Dr. Bean said that many fabrics in the proofing trade are dyed with "wood" shades. These shades might be susceptible to dilute alkali and it sometimes happens that the garments become reddened when they have been made wet with rain. This is due to the solution of traces of alkali from the proofings, which become concentrated on drying in the cotton fabric. A similar effect might be brought about by splashing with alkaline street mud. The tendency for the cloths to redden is reduced by very thorough chroming in the dyeing. The reddening of the cloths, he continued, must not be confused with a rather similar change of shade which is sometimes found in the neighborhood of the buttons on a mackintosh or other garment. Many buttons are made of synthetic resins whose preparation involves the use of formaldehyde. They often retain traces of formaldehyde, and as many dyestuffs are changed in shade by this substance damage might ensue. To neutralize the formaldehyde it is the custom of some button makers to treat the buttons with bleaching liquor. This is satisfactory if all traces of the oxidizing agent are washed away but it sometimes happens that traces are left, particularly in the holes, and the consequence is rapid rotting of the button thread.

Perishing of the rubber proofing, with or without tendering of the cloth, is a common damage and is produced in many ways, Dr. Bean explained. When proofings are put upon bleached cloths in which traces of acid or chemic remains, the rubber might decompose rapidly and become hard and brittle, and the fabric discolored. In proofing by the "cold cure" method, sulfur chloride is used, and this, in favorable circumstances would generate hydrochloric acid, which might attack both proofing and cloth. Attention to details and proper neutralizing of the proofings will reduce the danger of this damage. Either over curing or under curing of the proofings will lead to rapid perishing and hardening of the rubber.

The curing of rubber might have a harmful effect upon the dyestuffs in the cloth. Many are changed in shade by the cold curing processes and some damaged by heat curing. Others bleed through the action of the rubber solvents. It is necessary, therefore, to choose colors suitable for the purpose and not to give the proofer any sort of cloth which one fancies would look well when proofed. One example shown by Dr. Bean was a portion of a black coat dyed with sulfur black and then heat cured. The heat had decomposed the sulfur black, with the formation of acid, and the fabric was severely tendered during stoving.

Decomposition in proofed fabrics might be brought about by various metallic compounds. For instance, both zinc and magnesium chloride exert a deleterious action upon the proofings, especially when heated. Copper and manganese compounds cause rapid deterioration first to a sticky state and then to a hard and brittle condition. This is particularly the case in cold-cured goods. The sources of copper are generally dyestuffs, copper salts used in after-treatment of dyes, and impurities in the proofing materials and cloths. Similarly, manganese might be traced to the same sources. The amounts necessary to cause damage are very small, because the metals act as catalysts. As examples, Dr. Bean showed several brown fabrics in which copper was found in the dyed cloth, and then some

(*Continued on page* 196)

Technical Notes from Foreign Sources

Oxygen Bleaching for Viscose and Viscose Mixed Weaves

Fritz Ohl—Melliand's Textil-Ber. 15, 555 (1934).—A very closely reasoned discussion of the whole subject, obviously, from the title, in favor of the oxygen bleach. The whole paper, as we have learned to expect from Ohl, is compactly written and definitely clear and convincing, and no general summary of his argument can well be made. But it seems worth while to quote certain statements which he makes toward the middle of the paper:—

"It has been established that, for viscose, a bleach with hydrogen peroxide can be carried through safely, if any addition of any kind of caustic alkali be avoided. On the other hand, it has been established, that an addition of waterglass, which at the same time is of value for the maintenance of a certain stability of the bath, and also produces an alkaline reaction in the bath, is not dangerous. One might easily assume, that an optimum limit, in reference to the favorable amount of alkali, might be determined upon the basis of the pH value. *This is not the case.* Equivalent bleaching baths were prepared, the whole series comprising more than one pH value, and containing different alkalies—caustic soda, caustic potash, ammonia, and waterglass. At the same pH value, and of course identical conditions of working, the greatest attack upon the fiber was found to take place with the first three alkalies. At the same pH value, the bleaching bath alkalized with the waterglass produced distinctly less damage to the fiber than did the other three baths. It is therefore perfectly plain, that at least not the alkali content alone is to be held responsible for undesirable side-reactions in the oxygen bleaching-bath, even though the unfavorable effect usually increases with increasing alkali-content.

As in other cases also, the waterglass exerts a corresponding protective-colloid influence, beside its stabilizing action upon the peroxide, which seems in this case to be conditioned by the alkalinity itself. This, however, is not true of waterglass alone. As shown by other experiments, similar protective-colloidal action is exerted by other compounds which may be added, principally colloidal substances, for example, sulfite liquor, vegetable starches, lecithin, etc., even when they are added in very small quantities. In all cases, such additions usually cause a decrease in the speed of reaction (rate of bleaching). It seems as though the protective action exerts itself not merely upon the tendency toward undesirable chemical action of the oxygen, but also upon possible undesired action of the alkali. Similar results are to be gathered from the experience of other lines of textile work. In view of the above, possible suspicions of the danger from more or less strongly alkaline bleaching baths ought at least to be somewhat less prevalent."

(The subject of oxygen bleaching has been rather to the fore during the past few years, judging from not infrequent references to it.)

Fatty Acid Condensation Products vs. Fatty Alcohol Sulfonates

Melliand's Textil-Ber. 15, 557 (1934).—The closing papers of a friendly polemic between Dr. Kurt Lindner and M. Muench, which has evidently been proceeding during the past year. Without expressing even a merely casual opinion as to which of the two authors has the best argument as to what we are dealing with in these new assistants roughly classified under the names given, we may venture the comment that there really is a serious confusion existing as to what the phrase "sulfonated" means, in reference not only to the fatty alcohols, but the saturated and unsaturated fatty acids, and the hydrocarbons (in which latter only does it seem to be properly used). Properly employed, the term sulfonation product has a meaning quite different from merely a sulfuric acid ester, and in most cases the reactions of the products, from the chemical side at least, should show which is which. On still other grounds, a term with a definite meaning ought surely to be used with that meaning only. In spite of confident statements made by self-constituted "authorities", many bona-fide chemists consider that we are as yet none too sure, even now, of what the real classification of the long-known and widely used "sulfonated" castor oils should be. There seems to be no reason why a term of such exact significance should not be used in that sense and in no other, and for this reason a sharp disagreement between good chemists such as the above is a healthy sign of a desire for the truth.

Dyeing of Acetate-Silk

German Patent No. 489,344 (*January* 17, 1930).—*I. G. Farben-Ind. A.-G.*—The process here considered is that of disperse dyeing, the compounds involved being non-acetylated amino-anthraquinones or their substitution products or homologues, not possessing any affinity for natural fibers, and being of weakly basic nature.

For example, 1-ethylamino-anthraquinone is dissolved in formic acid or ethylene chlorhydrine, or any other suitable solvent (which will mix freely with water when diluted), and the solution poured into a weak aqueous solution of Turkey-red oil. The anthraquinone derivative is thus precipitated and dispersed at the instance of precipitation, the degree of division of particle being very extreme. Dyeing of the fiber then takes place as usual.

Stable Diazo-Salt Pastes

German Patent No. 499,294 (*June* 5, 1930).—*I. G.*

Farben-Ind. A.-G.—The pastes whose preparation is here described have as their basis naphthalene 1-5-disulfonic acid. The compounds formed by addition of the sodium salt of this acid to strongly mineral-acid solutions or pastes of suitable diazotized amines are regarded as the naphthalene sulfonates of the diazo compounds. Such salts do not appear to have been described as yet in the literature. They may also be prepared by addition of the free disulfonic acid to the weakly mineral-acid solutions of the diazo-compounds. They seem to be acid salts; they form more or less strongly colored crystalline powders, whose aqueous solutions are strongly acid toward Congo paper, so much so, that they can be titrated with standard caustic solution with Congo Red as indicator. They can also be neutralized, e. g., with magnesium or zinc oxides, calcium hydroxide, alkali carbonate or bicarbonate, so that, when finally dissolved, the solution will be ready at once for use as a coupling bath. The color of the acid salts is often different from that of the neutral salts; e. g., the acid naphthalene disulfonate of diazotized 3-nitro-4-aminotoluene is a pure green, while the neutral salt is yellow.

The solubility of the salts (particularly the acid salts) varies, according to the diazo salt involved; yet in any case it is sufficient to enable a deep penetration and rapid coupling, e. g., in the Naphthol AS process. The solubility of the salts may be increased by mixing them with metallic salts of certain aromatic sulfonic acids.

For diazo-salts, the products are remarkably stable (of course, no diazo salt ought to be treated carelessly). The dyeings from them, for example, in the Naphthol AS process, are as full and clear as with freshly diazotized and otherwise untreated diazo salts.

Printing with Vat Colors

German Patent No. 495,712 (*April* 22, 1930).—*I. G. Farben-Ind. A.-G.*—The process here protected consists in making up the vat dyestuff into a suitably thick paste with a solution of cellulose esters or ethers, printing this paste upon the weave, and after-treating with a reducing agent and alkali, to reduce and fix the vat dyestuff, which is then developed by oxidation as usual. A subclaim specifies the use of water-soluble esters or ethers of cellulose. By the reduction in presence of alkali, the esters or ethers are thrown down upon the fiber ("salted out"), and so prevent bleeding of the color into the surrounding areas. Ordinary thickeners, as starch or gum pastes, cannot be used, as they would be broken down by the alkali, lose their viscosity thereby, and allow the color to bleed. By the method here given, the printed goods may be dried and stored, to be fixed later—they do not have to be worked up at once.

The use of vat colors, made up in a gum-starch paste with reducing agents and alkali, are not suitable for printing with the high-relief, photo-engraved rolls now often being used for fine work, since the dyestuff cannot be incorporated in sufficient amounts to give a good effect with the delicate patterns of line-work often involved. The present method, however, is well suited to that method of printing, since much more dyestuff can be incorporated with the "paste" or ester or ether. The effects so obtainable are very beautiful and artistic.

Sulfur Dyestuffs

German Patent No. 489,086 (*January* 13, 1930).—*I. G. Farben-Ind. A.-G.*—The process here patented consists really in further elaboration of sulfur dyestuffs already formed, for example, those dyestuffs covered by the specifications of German Patents Nos. 477,698 and 478,-351. If such products, either in substance or dyed upon the fiber, are boiled in aqueous solution with alkylating, aralkylating, or arylating agents, in the presence of a little alkali and a reducing agent, the new products are formed. If the mixture is only warmed, the reaction is prolonged, or may even not take place at all. A suitable substituting agent is dimethyl-benzyl-phenyl-ammonium chloride (the addition-product obtained by heating benzyl chloride with dimethyl-aniline); the reducing agent is hydrosulfite by preference.

Five examples are given.

Vat Dyestuff (Pyrazol-Anthrone Series)

German Patent No. 493,813 (*March* 14, 1930).—*I. G. Farben-Ind. A.-G.*—The procedure protected by this patent consists, generally speaking, in condensing pyrazol-anthrone with 1-amino-2-halogeno-anthraquinones, or their substitution-products, in the heat, in the presence of alkaline condensing agents. Catalysts may be used also or not, as desired. The products are vat dyestuffs of great tinctorial power, and of good fastness-properties.

It appears, from the properties of the products, that the condensation involves not only the splitting out of the 2′-halogen of the amino-anthraquinone with the imide hydrogen of the pyrazol-anthrone, but also a condensation between the 2-hydrogen of the pyrazol-anthrone and the 1′-amino-group of the amino-anthraquinone, resulting apparently in the formation of an imino group between these points, with elimination, somehow, of hydrogen.

Two examples are given.

Reserves Under Insolubie Azo Dyeings

"X."—TIBA 11, 347 (1933).—A description of a method patented by the Societe pour l'Industrie Chimique of Basel (French Patent No. 739,810), the point of which lies in the use of xanthogenates as the principal active agent.

The xanthogenates, the reviewer says, are very suitable for the production of white or colored reserves under insoluble azo dyeings, dyed by the usual method of padding and developing. The process can be carried out conveniently, by printing solutions of xanthogenates, properly thickened (i.e., pastes containing xanthogenates) upon the goods, which have already been padded with the passive azo component, and then developing the ground color as usual, by passage through a bath of a diazotized amine.

In this way, pure white reserves are obtained. One may also print on the xanthogenate in paste first of all, and then pad and develop the ground as usual.

There is a large number of second or passive components available for such a process; beta-naphthol, the Naphthol AS series of products, the arylides of other acids, such as the carbonic acids of hydroxy-carbazole, hydroxy-phenanthrene, hydroxy-diphenylamine, and the hydroxy-anthracenes: those substances containing the —CH_2—CO— grouping, such as the pyrazolones and their derivatives, the derivatives of acetacetic ester; the 1-naphthol-4-aryl-ketones (one is referred to later as "benzoyl-1-naphthol"), the arylides of the single-ring hydroxy-acids, etc. Of the amines already in use, or suitable for use or more extended use, are aniline and its various substitution-products and homologues, as the chlor- and nitro-anilines and toluidines, and the chlor-nitro-derivatives, the mono-acylated phenylene-diamines and toluylene-diamines, the amino-diphenylamines, the naphthylamines, the amino-anthraquinones, amino-carbazoles, the amino-azo-compounds, etc.—a very large selection upon which to draw for various possibilities of color-effect.

As the xanthogenates, those preferably employed are the salts of the alkali metals (merely because such salts are the most easy to prepare); but other xanthogenates may also be employed, e.g., the xanthogenates of lead or tin, of magnesium or aluminium. Such salts of the heavy, or at least non-alkali metals, are best prepared by double decomposition of the alkali xanthogenates with appropriate salts of the heavy metal, in the printing paste itself.

Colored reserves may be produced by incorporating in the xanthogenate paste dyestuffs which will fix themselves upon the fiber without affecting the action of the xanthogenate upon the ground color. The basic and the vat dyestuffs are particularly suitable for this purpose, the vat colors being capable also of being applied in the form of their leuco-derivatives or as their leuco-ester salts. The leuco compounds of the vat dyestuffs are developed in the usual way, after the ground azo color has been developed.

Several examples are given:—

(1)—The weave is padded with a solution containing 12 g. of Naphthol AS, 10 cc. of caustic soda solution of 36° B., 15 cc. of Turkey-red oil of 50 per cent, in 300 cc. of hot water, and then made up to a liter. The cloth is then dried, and printed with a reserve composed of 125 g. of 1/1 gum solution, 50 g. of potassium xanthogenate, and 50 cc. of water. The goods are then dried, and developed with a diazo-solution of 4-chlor-2-amino-diphenyl ether. In this way, white effects upon a red ground are obtained.

(2)—The goods are padded as in (1), and printed with a paste made up of 12 g. of Indigosol O4B and 50 cc. of water, which are warmed together till homogeneous, then cooled and mixed with 125 g. of 1/1 gum solution, and 50 g. of potassium xanthogenate. The goods are developed with a diazo bath prepared from 12 g. per liter of 4-nitro-3-6-dimethyl-1-amino-benzene, and then passed immediately through a bath containing 5 g. of sodium nitrite and 20 cc. of HCl of 22° B. per liter, to develop the Indigosol. Blue effects upon a red ground are obtained.

(3)—The goods are padded with a solution containing 15 g. of benzoyl-1-naphthol (see note upon this, above), 15 cc. of caustic soda solution of 36° B., 15 cc. of Turkey-red oil of 50 per cent, these made up together with 300 cc. of boiling water, and diluted to a liter; and then printed with the following paste: 135 g. of gum solution 1/1, 12.5 g. of Ciba Blue 2BD paste, 12.5 g. of potassium carbonate, and 10 g. of sodium hydrosulfite are warmed together till homogeneous, then cooled, and mixed with 50 g. of potassium xanthogenate. After printing, the goods are steamed for three to four minutes in the Mather-Platt, and developed in a solution containing, per liter, 12 g. of diazotized 4-chlor-2-amino-diphenyl ether. The effect is again blue upon a red ground.

(4)—The goods are padded with a bath prepared thus: 12 g. of Naphthol AS, 18 cc. of caustic soda solution of 36° B., and 15 cc. of Turkey-red oil of 50 per cent are mixed with 300 cc. of hot water, and 12 g. of Katanol O stirred in, then diluted to a liter. The goods, after padding in this, are dried, and printed with a paste made up of 2.5 g. of Methylene Blue D, 5 cc. of alcohol, 45 cc. of water, 125 g. of gum solution 1/1, and 50 g. of potassium xanthogenate. The goods are then developed, as to ground, in a diazo-bath prepared from 10 g. of 4-chlor-2-amino-diphenyl ether per liter, then dried and soaped. Again, blue effects upon a red ground are obtained.

(5)—The goods are padded with a solution containing, per liter, 25 g. of aceto-acetic o-tolidide, 20 cc. of a solution of caustic soda of 36° B., and 20 cc. of Turkey-red oil of 50 per cent. The goods are then printed with a reserve prepared as in (1), and developed in a bath containing, per liter, 15 g. of m-nitro-p-toluidine, diazotized as usual. The effect obtained is white upon a yellow ground.

(6)—The cloth is padded as in (1), with 12 g. of Naphthol AS per liter, as usual, and printed with the following paste: 125 g. of gum solution 1/1, 50 g. of potassium xanthogenate, 40 g. of zinc chloride, and 50 cc. of water. After drying, the color is developed in a bath containing 24 g. of diazotized 4-amino-4'-ethoxy-diphenylamine. Whites upon a black ground are obtained.

(7)—The weave is padded with 15 g. per liter of Naphthol AS-BL, prepared as usual, then printed with the reserve of (6), and developed in a diazo-bath of 12 g. per liter of 5-nitro-2-anisidine. Whites upon a brown ground are obtained.

Soluble Starches and Their Utilization

Gustav Durst—Monats. f. Textil-Ind. 48, 213 (1933).—The first part of this paper has already been noted in these columns.

(*Continued on page* 195)

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

APRIL 6, 1936

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Standard Wash Fastness Samples

Cotton, Wool, Silk

The standard samples which have been in preparation for some time by the Sub-Committees on Fastness to Washing of Dyed Cotton and Dyed wool are now ready for distribution, and the original standard silk sample cards have been revised to correspond with the new system of classification first introduced in the 1934 Year Book.

These standards have all been carefully dyed with the dyestuffs and according to the dyeing methods recommended in the 1934 Year Book and each set includes a dyeing representing each of the different classes of fastness.

With these sample dyeings for reference it will be possible to accurately grade the fastness to washing of any dyed cotton, wool, or silk fabrics, by comparing them with the standards after subjection to the standard washing tests as approved by the Association.

The A.A.T.C.C. is now prepared to furnish these three sets of washing standards for $1.00 per set which is to cover the cost of preparation.

All inquiries concerning these washing standards should be addressed to the Chairman of the Research Committee.

LOUIS A. OLNEY,
LOWELL TEXTILE INSTITUTE,
LOWELL, MASSACHUSETTS.

Proceedings of the American Association of Textile Chemists and Colorists

Problems Involved In Finishing Heavy-Weight Silk and Rayon Fabrics*

By DWIGHT L. JOHNSON†

THE subject of my remarks tonight—"The Problems Involved in Finishing Heavy-Weight Silk and Rayon Fabrics"—seems to be an ambitious attempt to solve, in a short time, difficulties which have been prevalent in the industry for many years.

An intensive study of this problem shows a natural division which automatically classifies these difficulties into two distinct groups—

1. The classification into which we could put those phases of manufacture over which the dyer has no control.
2. The classification under which we put the difficulties that develop in boil-off, scouring, dyeing and finishing operations—processes over which the dyer has a very definite control.

We, in the Textile Research Department of Procter & Gamble, have an opportunity to view the problems you daily encounter from a different perspective. This is because our experiences, both practical and from a research angle, are not confined to a single plant or laboratory. These practical experiences, supplemented by intensive laboratory research, enable us to draw conclusions which we hope you will find of interest.

Factors Over Which the Dyer Has No Control

First, let us look at those phases of manufacturing which are beyond the control of the dyer. These are raw materials, throwing, and weaving and copping.

CHART I

Raw Material, Throwing, Weaving and Copping Faults

A. SILK

Raw Material	*Throwing*	*Weaving and Copping*
1. Mixed Natured Silk	1. Mixed Filaments	1. Metallic Soap from Harness, Cops, Heddles and Reed
2. Mixed Sizes	2. Mixed Yarns	2. Wrong Twist
3. Old Silk	3. Improper Soaking	3. Shuttle Tension Variations
4. Raw Defects— Lousy Uneven Fuzz Loops Hairy Poor Quality	4. Uneven Twist	4. Dropping of Ends and Picks
	5. Humidity Variation	5. Faulty Construction
	6. Varying Tensions	
	7. Exceeding the Elongation and Elastic Limits	
5. Construction	8. Cut or Weakened Yarns	

B. RAYON AND ACETATE

1. Mixed Filaments	1. Inadequate Soaking	1. Sizing Materials
2. Mixed Rayon or Acetate from different Plants	2. Improper Sizing	2. Metallic Soap from Harness, Cops, Heddles and Reed
3. Variations in Dyeing Characteristics	3. Variation in Yarns	3. Wrong Twist
4. Mixtures in Manufacturers Products	4. Twisting While Damp	4. Shuttle Tension Variations
	5. Humidity Variations	5. Dropping of Ends and Picks
		6. Faulty Construction

Chart I enables us to discuss raw materials, throwing, weaving, and their contributing factors in their logical order. Our remarks will have to be brief since the difficulties are many and our time restricted.

RAW MATERIALS

Silk

Mixed Natured Silk

Few, if any, satisfactory tests are conducted to ascertain the nature and dyeing characteristics of raw silk used in the manufacture of crepe materials. Experiments show that when yarns contain an unbalanced number of hard or soft natured filaments, streaked dyeings result. While the relative amount of yarn containing both hard and soft filaments is comparatively small, it takes little more than a trace in the total poundage used to cause disastrous results.

Raw Mixtures

Variations in shade of dyeings are often caused by mix- of 13/15 and 20/22 raw silk woven into the same piece. The degree of shading depends on the color used—browns, greens and blues, usually showing more marked differences than other colors.

Old Silk

Occasionally, the Japanese and Chinese Governments, brokers, dealers and manufacturers, store raw silk and yarn for prolonged periods. When this "old silk" is finally put into circulation, it sometimes becomes mixed in fabrics with fresh silk. It takes longer to remove the sericin from the aged silk than from the new silk. This may result in uneven boil-offs and different degrees of coloration on dyeing.

Raw Defects

The poorer grades of raw silk show lousiness, unevenness, fuzziness, loops and hairiness. These defects may be partially eliminated or minimized in the cleaning and spinning operations. However, they are never entirely removed and their presence is evident in many finished pieces. The true solution of difficulties arising from such defects is more rigid testing and analysis of the raw silk.

Rayon

In general, the problems we have listed under Raw Silk are also applicable to Rayon and Acetate. However, there are a few additional points encountered, especially in processing, that pertain to artificial fibers.

*Presented at meeting, New York Section, Oct. 4, 1935.

†Textile Research Dept., Procter and Gamble.

Mixtures of like rayons, from the same manufacturer but from different plants.

Mixtures of different filament and denier yarns.

Mixtures of different brand yarns.

Mixtures of yarns can usually be traced to the weaving process and are difficult to "spot" in the fabric until they show up as uneven shrinkage or as streaky or variegated dyeings.

THROWING

Silk

Mixed Raw Materials and Yarns

Yarns of different sizes and blends are occasionally mixed, due to insufficiently distinctive tints, raw mixtures, and other numerous reasons.

Soaking Faults

It is not possible to obtain smooth threads of uniform diameter, with even turns and properly meshed or twisted without beading, unless the raw silk has been soaked in such a manner that it is soft, flexible and pliable. In short, the individual thread must be carefully processed to accept and withstand the subsequent twisting operations. Incorrect soaking methods and the use of improper soaking materials produce non-uniform threads which, in turn, result in a fabric difficult for even the best dyer to finish.

Uneven Twist, Humidity Variation, Different Tensions and Elastic Limits

These four factors are responsible for producing yarn that varies in size, elasticity and turns, which affects the creping qualities and dye shade of the fabric.

Weakened Yarns

Many unsatisfactory results which apparently originate in the boil-off, scouring or dyeing operations, can be traced directly to throwing conditions. Mildew growth, the use of improper soaking ingredients, poor storage conditions, and nicked metal bobbins, cause weak yarns and, subsequently, dyehouse troubles.

Rayon and Acetate

An analysis of an unsatisfactory rayon fabric may show inadequate soaking, improper sizing, yarn variations, twisting while damp, and differences in humidity.

WEAVING AND COPPING

Silk and Rayon

Metallic Soaps

Metallic soaps formed during weaving and copping are responsible for a high percentage of the undesirable results on the finished fabric. Yarns impregnated with soaps, sulfonated oils and free fatty acids in contact with metal harness, reed and cops, frequently form insoluble soaps which subsequently resist scouring or degumming, and later act as resists to proper dyestuff penetration. Finally, they are evident in the finished fabric as light and dark sections or streaks.

Wrong Twist, Shuttle Tension Variations, Dropping of Ends and Picks

All or any of these produce woven fabrics that contain density variations, which materially affects the absorption and reflection of the light. On dyeing varying shades result.

Faulty Construction

Each fabric construction tends to produce a characteristic fabric finish. Manufacturers often expect the dyer to produce a certain crepe or finish on a fabric which was doomed to be a failure before it left his weaving department. Such failures are often due to faulty construction.

Factors Over Which the Dyehouse Has Control

Up to this point, we have discussed only those phases over which the dyehouse has no control. Now, let us look at Chart 2. Here we have outlined those faults which take place in the scour, boil-off, dye and finishing operations—those factors which the dyer can control.

CHART II

Boil-Off, Scouring, Dyeing and Finishing Faults

A. *SILK*

Boil-Off	*Dyeing*	*Finishing*
1. Improper Preparation.	1. Improper Handling	1. Poor Selection of Finish
2. Careless Handling	2. Delayed Rinses	a. Odor
3. Insufficient Soap Concentration	3. Metallic Soaps	b. Discoloration
4. Excessive Agitation	4. Hard Water Soaps & Oil Spots	c. Poor Hand
5. Insufficient or Excessive Boil-off Time	5. Poor Choice of Dyestuffs	d. Oil Separation
6. Selection of Detergent	6. Surface Dyestuffs	2. Excessive Use of Finish
7. Action of Alkalies	7. Improper Dyeing Technique	
8. Oil Spots	8. Penetrants	
9. Hard Water Soaps		

B. *RAYON & ACETATE*

Boil-Off	*Dyeing*	*Finishing*
1. Improper Preparation	1. Improper Handling	1. Hand Desired
2. Incorrect Scouring	2. Delayed Rinses	2. Poor Selection of Finish
3. Poor Scouring Agents	3. Metallic Soaps	a. Odor
4. Embossing	4. Hard Water Soaps and Oil Spots	b. Discoloration
	5. Poor Choice of Dyestuffs	c. Poor Hand
	6. Improper Dyeing Technique	d. Oil Separation
	7. Oil-Rust Spots	

BOIL-OFF AND SCOURING

In our opinion, the real foundation of satisfactory dyeing and finishing is proper boil-off or scouring. The method used in preparing the fabric for the boiling off and scouring operations determines, to a large extent, whether we are to get good results.

Silk pieces can either be suspended from strings or hung over poles, depending upon the weight and type of the fabric. Regardless of the method used, however, the fabric weights should be uniformly distributed and precautions taken to see that the folds of the fabric are in a receptive condition for good penetration of the liquor.

In boiling off heavy weight silk and in scouring heavy weight rayon fabrics, too low a concentration of soap may handicap the subsequent dyeing operation. Throwster's oils and other foreign matter are not dispersed properly and, as such, may settle in the folds of the cloth. When

the sericin and silk tints are unevenly removed, it results in non-uniformity in the finished pieces.

Prolonged and excessive agitation in the boil-off bath usually means chafe marks, bruises and an excessive number of open filaments. The extent of damage from this source is usually in proportion to the rubbing that the materials received due to overcrowding or to excessive motion of the pieces by either the operators or by open steam coils.

Insufficient or an over-boil-off is also the cause of poor results. Insufficient time results in gum spots, streaks, light and dark places, any or all of which may require the re-processing of the entire load. On the other hand, too long a time in the boil-off bath produces fabrics which are equally unattractive, although the results are different. In this instance, the hand is dry and harsh and the fabric, in addition to showing chafe marks, gives the appearance of being brittle and materially weakened.

Many difficulties can be eliminated by a proper boil-off operation. A proper boil-off in turn is definitely governed by two factors—

1. The correct procedure.
2. The boil-off agents.

The best possible procedure can be ruined by the use of an ineffective or unsafe degumming agent. Likewise, the use of even the best agent will not produce a good job without following out a proper procedure. The procedure varies naturally with the fabric and the plant but the boil-off agent is not so variable a factor.

Many laboratory and plant tests run over the past several years, have proven that the degumming media which gives most economical, safe and consistently satisfactory results, is low titered, flaked oleate soap, which contains the highest possible percentage of liquid oils. This high percentage of liquid oils provides a real factor of safety because of lower rate of hydrolysis which gives mildness of action on the fibers and assures freer rinsing. The lower the titer of the soap the safer the degumming operation. This is especially true where the fabrics are to be subsequently tin or lead weighted. In order to thoroughly and efficiently degum silk fabrics of heavy quality, at least 25% of a good quality, flaked soap is necessary. Lower percentages of soap prolong the boil-off and necessitate excessive handling, thereby contributing to chafe, broken filaments and bruises. Also, the boil-off emulsion is not stable, and insoluble soap curds, throwing oils, scum and other foreign matter precipitate on the cloth. Such foreign matter is extremely difficult to remove in the rinsing operation and shows up on the dyed fabrics as spots and streaks.

Occasionally, we find those who try to reduce their boil-off time by the addition of alkali. Experience has taught us that the use of alkalies, such as sal soda or soda ash, in the boil-off bath, does not necessarily injure the fiber, providing it is used judiciously and in relatively small quantities. Recently we analyzed a series of boil-off compounds and soaps that were offered to the various trades of the silk industry. As is usually the case, analysis revealed that a good percentage of these boil-off compounds depended primarily on strong alkalies for their efficiency. Such products are actually dangerous and have no place as a degumming agent for silk fabrics.

The selection of a boil-off soap is just as important when processing acetate fabrics or mixed fabrics containing even a small percentage of acetate. Acetates and alkali don't mix,—they just don't like each other. When acetate and anything but the mildest of soaps come in contact, the acetate fiber is converted back to regenerated cellulose which is more generally described as rayon. Thus the desirable characteristics of acetate—the handle, the appearance, the dyeing characteristics, etc., are modified or completely lost.

In general, conditions that produce satisfactory processing on silk fabrics are of equal value when applied to rayon and acetate processing. However, there are several points we will mention which, in our opinion, are particularly applicable to the artificial fibers.

1. Care should be taken to prevent rayons and acetates from becoming wrinkled or distorted prior to the scouring operation. Such wrinkles will remain throughout the scouring and dyeing operations and will be readily apparent in the finished fabric.

2. Superior results are usually obtained on rayon and acetate fabrics by dispensing with both strings and poles and by scouring them in a continuous machine in the open width form. Such a machine will scour economically and successfully 35 to 50 pieces per hour, using either soap or fatty alcohol sulfates. This procedure is to scour the rayon or acetate fibers in a 5 bowl continuous machine, with the first three bowls at 180-212° F., each containing 1% soap or 0.1% of the fatty alcohol sulfate solution, and the last two bowls consisting of rinse waters at 180° F. and cold. It is a known fact that these high temperatures are dangerous, even ruinous, to acetates when alkali is present. Therefore, the selection of a safe, low titered soap, or sulfated alcohol, is of utmost importance to assure getting the full measure of value of the acetate. Acetate scoured open width with the fatty alcohol sulfates possess a distinctly superior hand to those processed with soap. Penetration is better, the hand is softer, the colors are brighter, and more level dyeings are obtained.

DYEING

When silk, rayon and acetates have been properly prepared, satisfactory dyeing results can usually be obtained by the use of the right dyestuffs and a good surface active agent which combine wetting, penetrating and levelling properties.

Frailly constructed cloth cannot stand jerking or tugging when on the dyebacks. Water levels should be carefully controlled. If the water level is low, the folds of the fabric may drag against the sides and bottom of the dyetub

or the pieces may crowd and become entangled, all of which result in excessive wrinkles, streaks, break marks and open fibers.

Another important point too frequently neglected is the value of rinsing promptly after the boil-off or scouring operation. Some mills allow the degummed or scoured fabrics to be piled carelessly on trucks that are bumped and rubbed together and later are pushed to one side. Under such conditions, capillary action may take place, thereby producing a blotchiness consisting of yellowish brown streaks which are extremely difficult to remove or cover up in dyeing. This undesirable condition is easily avoided by routing the pieces promptly from one process to the next or by drying the pieces between operations.

Metallic soaps also cause trouble in the dyehouse. These may have formed in the soaking, weaving and copping operations, or in the dyehouse. The metallic soaps which form in the dyeing operation due to the reaction of soap or sulfonated oils with the calcium or magnesium in the water, usually appear as blotches, tiny dark spots or niggerheads. The metallic soaps formed in contact with cops, heddles, etc., appear as dark streaks running from selvage to selvage often as frequently as every 8 to 14 inches throughout the length of the entire piece. Too often this trouble is mis-classified. Sometimes the throwster is blamed for uneven twist and varying tensions while actually the streaks are caused by the presence of an insoluble soap.

When metallic soaps are encountered in the plant, they can be eliminated by first stripping the pieces, then treating in a 1% oxalic acid bath at 180° F. for 15 to 20 minutes, and finally rinsing, soaping, and re-dyeing.

An important characteristic to be observed in the selection of dyestuffs is their rate of exhaustion. If the dyestuffs have a tendency to exhaust rapidly, dye deposition may be uneven and blotches, streaks and variations in shade may result. Information regarding the proper dyestuff, when it should be added and how the best results can be secured, can be obtained from the service department of your dyestuff supplier.

Many types of fabrics, especially heavy fabrics or those containing tightly twisted yarns, when dyed with certain dyes, require the addition of a wetting, penetrating, or levelling agent, in order to obtain best results. We know of no better assistant than 0.25% of the fatty alcohol sulfates, used alone or in conjunction with sulfonated castor or olive oils. The use of from 1% to 2% of a low titered flaked soap is also a very satisfactory assistant for the dyeing process.

The precautionary measures applicable to dyeing silks also apply when dyeing heavy weight rayon and acetate fabrics. The problems and the causes of trouble are similar.

FINISHING

Providing the processing has been properly conducted up to this point, the remainder of the problem, that of applying sufficient finish of the proper quality to obtain the desired hand and finish, is relatively easy.

Care should be exercised to select oils that will not change appreciably upon standing or aging. Fluctuations in pH, oxidation, hydrolysis and tendency to separate, frequently cause discoloration and odors to develop on the cloth, thereby affecting the shade and strength of the dyed pieces. When blended oils are used, only those should be selected which will not separate. Otherwise, preferential absorption may take place and the oiled fabrics will show variations in shade from piece to piece or even within the same piece.

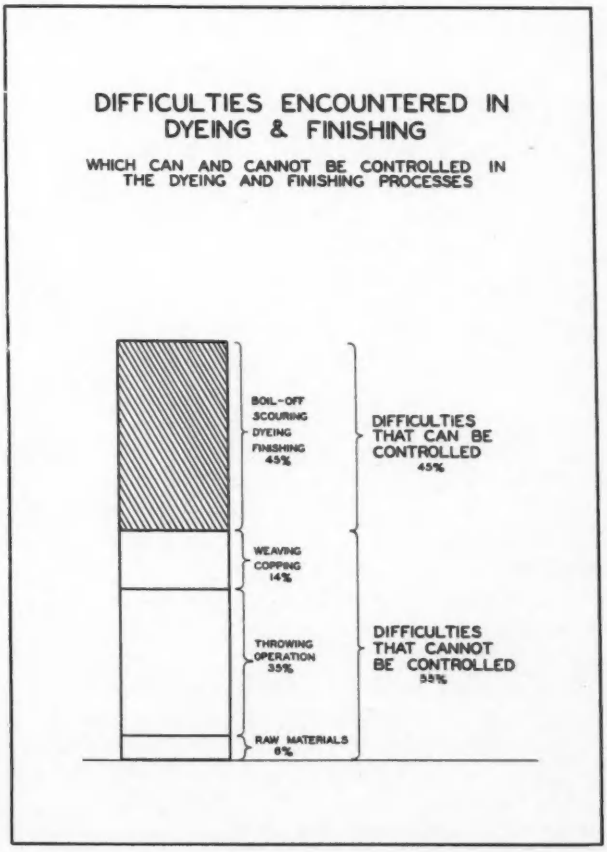
Up to this point we have considered our problem as two distinct phases that we classify originally as—

First—Problems over which the dyer has no control.

Second—Difficulties that develop in the dyehouse and over which the dyer has a very definite control.

Now, let us summarize these problems by studying Chart III.

CHART III



Under these three classifications—Raw Materials, Throwing, Weaving and Copping—we have illustrated the percentage of your difficulty that can be classified in the first division. At the top of the chart under dyeing, we have placed those phases that fall in the second classification.

Here we have raw materials contributing 6%; throwing, 35%, and weaving and copping, 14%—totalling 55% over which you as dyers and finishers have little, if any, control.

Probably the question in your mind is—"Well, what can we do about difficulties originating in Raw Materials, Throwing, Weaving and Copping?" Unfortunately, the answer is practically nothing in so far as correcting them in your own dyehouse is concerned. However, if you are a one unit organization you should find it comparatively easy to secure proper cooperation between departments and by so doing, lighten the burden of all concerned. Commission dyers can possibly secure the help and cooperation of their clients in ascertaining the cause of their difficulties by discussing them with the raw silk and rayon fabric manufacturers. Since this is your only way of eliminating or minimizing these uncontrolled factors, a campaign to reduce this 55% of your problem will very likely prove profitable.

Now, let us look at the 45% of your troubles that constitutes the second phase of our talk. These originate in the Boil-Off, Scouring, Dyeing and Finishing operations. These are your responsibilities. A thorough investigation of the supplies you are using, your plant supervision, and your procedure will do much to lower this figure. Finally, minimize your troubles by using only dependable reliable chemical supplies such as dyes, finishes and soaps.

I would like at this time to thank you personally, and on behalf of the Textile Research Department of the Procter & Gamble Company, for this opportunity to discuss with you these problems.

DISCUSSION

Chairman Freedman: Gentlemen, you have just heard a very interesting and instructive paper on causes of troubles, and I am going to reserve to myself the right to say something later on. I will call on Mr. Baxter to lead the discussion.

Mr. Baxter: I don't think we are going to have any trouble in getting a good deal of discussion on the picture that Mr. Johnson has presented. I was not at all sure that I was going to be able to be here myself. I certainly am glad that I was able to make it and listen to this very excellent talk. I am only sorry that a good many of the converters and customers with whom I do business are not here. (Laughter).

I will have to get hold of one of these charts and carry it around, so that when I am shown a few of these little spots or a little bar mark—which we see almost every day in the week—I won't feel quite so ignorant when I have to admit I can't look at the piece and tell just exactly what is wrong.

There is only one thing that I would like to ask in regard to the last chart: Was that drawn up, combining both silk and rayon fabrics?

Mr. Johnson: Yes, that is right.

These charts represent a classification of all our associations with problems involved in finishing heavy weight silk and rayon fabrics.

Mr. Baxter: I imagine there would be some material differences in the percentages in silk as compared to rayon.

Mr. Johnson: Yes, possibly some slight discrepancies. However, we did not feel that the differences were great enough to justify additional charts.

Mr. Baxter: On your first chart, you said that the knit goods people had to have a very complete picture and make thorough tests in order to make sure they were getting the proper material; that doesn't necessarily follow in the weaving. I think that is is a mistake. I think the plants only think that they don't have to have it, and that they would all be better off if they did have it.

I know that there are many here who would like to ask questions in connection with this. I would like to start some discussion by having some of the members get up and ask questions.

Mr. Decnyf: Have you had any experience with tinsel fabrics? We quite frequently have trouble with the tinsel tarnishing, and I would like to hear what your opinion is as to what some of the causes are.

Mr. Johnson: I am afraid that I can't attempt to answer that until I find out how you start the processing.

Mr. Decnyf: For instance, if you have an acetate rayon fabric with some tinsel woven in with it, in many cases you will find that the grade of tinsel is not as good as it might be, but then, on the other hand, there are supposed to be some very good qualities of tinsel that are not supposed to tarnish but they do. What are some of the possible causes of that?

Mr. Johnson: May I ask you, in processing these fabrics prior to the dyeing stage, do they come in contact with soaps?

Mr. Decnyf: Yes, you usually have to give them a scouring, in order to get rid of the sizing which is in the piece, and in the case of silk, the silk is woven in the raw state and you have to give it a regular degumming boil-off.

Mr. Johnson: We have encountered those on silk materials, not on the rayons.

One explanation is that you may get a metallic soap deposit around the outer surface of your tinsel; even if it is only an infinitesimal amount, you will get a general dulling. To avoid such a condition we would suggest you try some of the sulfated alcohols, alone or in combination with a lower percentage of soap or alkali. This will tend to minimize the reaction.

Mr. Decnyf: You would say, try to keep away from any materials that would leave a fatty acid deposit in the cloth?

Mr. Johnson: That is right.

However, you may find that if you subject your materials to an after-treatment with a one percent solution of potassium cyanide, you will bring the tinsel back to a nice brilliance, and that is what you are probably interested in securing.

Mr. Decnyf: That is quite possible, but in many cases it is so badly corroded that by the time the cyanide reaction has really removed the oxide, or the tarnish, you have very little tinsel left.

Mr. Johnson: Yes, that is true. We should actually seek to eliminate the cause.

Mr. Decnyf: Yes.

Mr. Johnson: I would suggest that you try to get away from supplies containing free fatty acids which would react with your metals. Try something along the lines of the sulfated alcohols, and see what results you get.

Mr. Decnyf: How would the reaction to any sulfur compounds show up?

Mr. Johnson: I imagine you would get a dulling, a blacking effect, especially if the baths or cloth are on the acid side when sulfur fumes are encountered.

Mr. Decnyf: Yes. One customer complained to us that the tinsel tarnished after contacting with rubber. I was wondering if you knew of any possibilities of rubber causing such trouble.

Mr. Johnson: I don't know.

Mr. Decnyf: Thank you.

Mr. Baxter: I am sure there must be a good many questions you want to ask. Apparently none of these folks ever have troubles, or if so, they have solved them. (Laughter). I might say, in connection with tinsel, that that is quite an involved subject, and you can probably discuss that all night (laughter) and still find more reasons that hadn't come up

Mr. Zisman: I would like to ask you, Mr. Johnson, in your experience in throwing silk, or any problems that have come up to you, has it ever been suggested that soaking in an acid bath might have some value, or is it practical?

Mr. Johnson: Yes, we have reviewed this subject.

There is a likelihood that the carrier tubes, needles, and other metallic parts of the knitting machine, might be detrimentally affected by subjecting them to acid treated yarns. As a matter of fact, we know of mills who tried acid soakings and who were forced back to the more orthodox soaking method. This was because the acid soaking increased the bill for needles, etc.

Mr. Baxter: Do you have any further questions you want to ask? If not, perhaps you have some that you want to ask, Mr. Freedman.

Chairman Freedman: I haven't any.

Are there any further questions concerning the discussion this evening? If not, I would like to say that if we were chartered to issue degrees, I think we would issue a degree of M.T.S. to Mr. Johnson. To those who are not initiated I would say that means Master Trouble Shooter.

I want to thank you, Mr. Johnson, on behalf of the New York Section. I know we have all benefitted very much by the presentation of your paper, not alone because of the subject matter, but the manner in which you presented the subject. I want to say that we shall always look forward to having you come here and tell us some more.

Proceedings of the American Association of Textile Chemists and Colorists

The Oxidation of Wool

The Effect of Hydrogen Peroxide

By ARTHUR SMITH and MILTON HARRIS†

The purpose of this investigation was to provide quantitative data showing the effect of oxidizing agents on wool as a basis for studying all processes in which wool is exposed to oxidation reactions. The work reported in this paper deals only with the effect of hydrogen peroxide.

Data are presented on the effects on wool of varying the concentration, temperature and pH of the hydrogen peroxide solutions and the duration of treatment. The main point of attack during oxidation is the disulfide group of the cystine in the wool. The extent to which the wool is oxidized bears a functional relationship to the decrease in the cystine content and to the increase in the alkali-solubility of the wool.

I. INTRODUCTION

IN practical wool processing such as bleaching, carbonizing, lustering, printing, chlorination and bromination for producing "unshrinkable" finishes, and in natural aging involving the action of light, air, and moisture, wool may become partially oxidized, the extent of oxidation depending on the severity of the conditions. The quantitative estimation of the oxidation is of great importance, since previous work[1] has shown that this oxidation increases the susceptibility of wool to deterioration by alkali treatments.

While there are several groups in proteins which may be attacked by oxidizing agents and alkalies, the evidence obtained from studies of the effects of these reagents on cystine [2, 3, 4, 5, 6, 7] indicates that the greatest effect is produced on the disulfide groups. However, Fruton and Clark[8] showed that the introduction of acyl groups into the amino groups of cystine greatly increases the oxidizability of the sulfur and its lability towards alkali. It is to be expected therefore that the reactivity of the disulfide group as it exists in the complex wool molecule will be very different from that of the disulfide group in pure cystine.

The present investigation was undertaken to obtain quantitative data showing the effects of various oxidizing agents on the disulfide groups in wool and on the susceptibility of the oxidized wool to deterioration by subsequent alkali treatment. The work reported in this paper deals only with the effect of hydrogen peroxide.

II. MATERIALS AND METHODS

White worsted yarn prepared from raw wool which had been extracted with Stoddard solvent and washed with water, but which had received no chemical treatment, was used in this work. The yarn was further purified by extraction in a Soxhlet apparatus with alcohol and ether for 6 hours each and then washed with water at 50° C. All of the samples were conditioned and tested in a room maintained at a relative humidity of 65 percent and a temperature of 23° C, with the exception of those which became so gelatinous during alkali treatment that equilibrium was not readily obtained by conditioning. These samples were partially dried in an oven at about 50° C for 1 hour and then dried to constant weight at 105° C. The weights of the oven-dried samples were corrected to correspond with the moisture content of the original conditioned samples. The conditioned, untreated wool contained 13.2 per cent of moisture, 14.3 per cent of nitrogen, 3.23 per cent of sulfur and 11.6 per cent of cystine.

The total nitrogen was determined by the micro-Kjehldahl method[9], total sulfur by the oxygen bomb method[10], and cystine by the Sullivan method[11].

Resiliency tests were made with a compressometer[1]. Breaking strength tests were made by the single-strand method on a pendulum-type machine, the yarn being tested while wet.

The stock hydrogen peroxide used was a 10-volume (3.03 percent) solution, about 0.005 N with respect to sulfuric acid and contained 0.3 percent acetanilide as a preservative.

In the experimental procedure, 4-gram samples of the wool yarn were treated with 400 ml. portions of hydrogen peroxide solution. The supernatant liquor was poured off, the wool washed in running distilled water until 10 ml. of the wash water would not decolorize one drop of a 0.75 N solution of potassium permanganate, and then conditioned. The susceptibility of the wool to deterioration by alkalies (referred to as alkali-solubility in this paper) was determined by treating about 2-gram portions of wool with 200 ml. of 0.1 N solution of sodium hydroxide at 65° C for 1 hour. The wool was filtered on a Büchner funnel, washed with about 2 liters of distilled water, and conditioned or dried as was necessary.

*This is the first paper of a series on studies on the oxidation of wool.

†Research Associates from the American Association of Textile Chemists and Colorists at the National Bureau of Standards.

Proceedings of the American Association of Textile Chemists and Colorists

III. RESULTS AND DISCUSSION

1. Effect of Varying the Concentration of Hydrogen Peroxide

Samples of wool yarn were treated for 3 hours at 50° C. with hydrogen peroxide solutions varying in concentrations from 0.1- to 10.0-volume. Two-gram specimens of each oxidized sample were then given the alkali treatment previously described. The effects of the treatments on the physical and chemical properties of the wool are shown in Tables 1 and 2. The results indicate that the oxidation treatment has caused no significant changes in wet breaking strength, resiliency or total sulfur content. Both the cystine and nitrogen contents decrease with increasing concentrations of peroxide and exhibit a fairly sharp drop between concentrations of 4- and 6-volume.

TABLE 1.

The effect on wool yarn of hydrogen peroxide solutions of various concentrations at 50° C. for 3 hours.

Concentration of H_2O_2		*Cystine content*	*Total sulphur*	*Nitrogen content*	*Wet breaking strength*	*Compressional Resilience*
Vol.	%	%	%	%	kg.	%
0.0	0.00	11.6	3.23	14.23	1.15	53
0.1	0.03	11.6	3.30	14.19	1.07	51
0.5	0.15	11.6	3.24	14.14	1.10	53
1.0	0.30	10.8	3.24	14.17	1.09	52
2.0	0.61	10.7	3.21	14.18	1.07	51
4.0	1.21	10.5	3.21	14.17	1.13	51
6.0	1.82	9.6	3.23	13.99	1.10	53
8.0	2.43	9.3	3.20	14.04	1.08	50
10.0	3.03	8.4	3.23	14.05	1.03	50

TABLE 2.

The effect of N/10 solutions of sodium hydroxide at 65° C. for 1 hour on wool which has previously been treated with various concentrations of hydrogen peroxide at 50° C. for 3 hours. See table 1 for the effect of the hydrogen peroxide alone.

Concentration of H_2O_2		*Loss in weight*	*Cystine content*	*Total sulphur*	*Nitrogen content*	*Wet breaking strength*	*Compressional Resilience*
Vol.	%	%	%	%	%	kg.	%
0.0	0.00	12.8	2.2	1.61	14.03	0.30	42
0.1	0.03	18.3	2.2	1.73	14.07	....	42
0.5	0.15	16.8	2.2	1.63	13.97	0.19	40
1.0	0.30	17.7	2.2	1.63	13.88	0.17	37
2.0	0.61	20.0	2.0	1.57	13.91	0.13	36
4.0	1.21	20.9	2.2	1.76	14.01	0.08	36
6.0	1.82	41.7	1.4	1.83	13.83	....	..
8.0	2.43	46.1	1.4	1.91	13.63	....	..
10.0	3.03	55.6	1.3	2.11	13.67	....	..

The alkali treatment greatly accentuates the differences produced by oxidation alone and shows an even more pronounced critical concentration of hydrogen peroxide between 4- and 6-volume. Whereas the oxidation alone showed no significant effect on the sulfur content, wet breaking strength and resiliency of the wool, the subsequent alkali treatment produced a considerable decrease in all three. The samples treated with peroxide solution of concentrations greater than 4-volume became so gelatinous during alkali treatment that they dried to horny masses and the physical tests could not be made.

The sulfur content of each of the alkali-treated samples which had been oxidized with peroxide solutions below concentrations of 4-volume is about one-half of the sulfur content of the original wool. This is in accord with previous studies on the effect of alkalies on wool[1] in which it was shown that on continued treatment with alkali, the sulfur content decreased and approached a constant value at approximately half the sulfur content of the original wool. The increase in total sulfur content of the alkali-treated samples which had been treated with peroxide concentrations greater than 2-volume may be attributed to the oxidation of a portion of the sulfur to a form which tends to resist splitting from the molecule.

The increase in the alkali-solubility of wool treated with increasing concentrations of peroxide is of special interest since it offers a simple and reproducible method for measuring the extent of oxidation. It is also of interest to note that the decrease in the cystine contents of the peroxide-treated samples bears a functional relationship to the loss in weight of the corresponding samples after alkali treatment. The curves in Figure 1 show graphically the relationship of decrease in cystine content of the oxidized wool to the loss in weight when the oxidized wool is subsequently treated with alkalies.

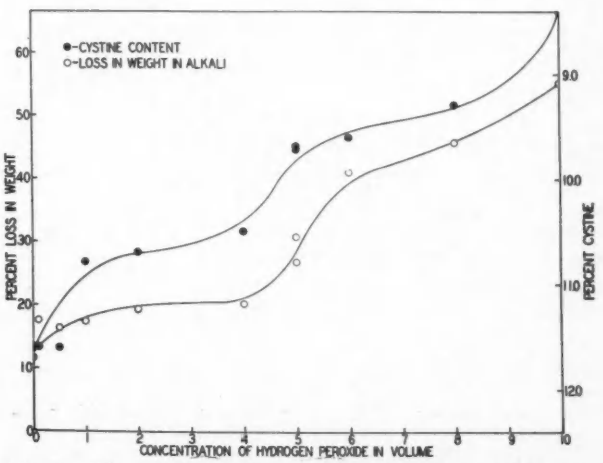


Fig. 1—Effect on wool of various concentrations of hydrogen peroxide for 3 hours at 50° C.

2. Effect of Varying the Temperature of the Hydrogen Peroxide Solutions

Samples of wool yarn were treated with 2-volume solutions of hydrogen peroxide for 3 hours at temperatures varying from 23° C. to 80° C. The cystine content and alkali-solubility of the oxidized samples were determined and are given in Table 3. The cystine content decreased and the losses in weight increased with increasing temperatures of the oxidized bath, the rate of change increasing rapidly above 50° C. The loss in weight in alkali appears to be the more sensitive measure of the degree of oxidation.

TABLE 3.

The effect on wool of 2-volume hydrogen peroxide solutions at temperatures varying from 23° C. to 80° C. for 3 hours and the alkali-solubility of the treated wool.

Temperature of H_2O_2 solutions °C	*Cystine content after treatment with H_2O_2* %	*Alkali-solubility* %
23	11.2	9.7
35	11.3	13.6
50	10.8	19.4
65	9.8	31.6
80	7.4	100.0

3. Effect of Varying the Duration of Treatment with Hydrogen Peroxide

Samples of wool yarn were treated with 2-volume solutions of hydrogen peroxide at 50° C. for periods of time varying from 1 to 20 hours. The effects on the cystine content and alkali-solubility of the wool are shown in Figure 2. While the cystine content decreases and the

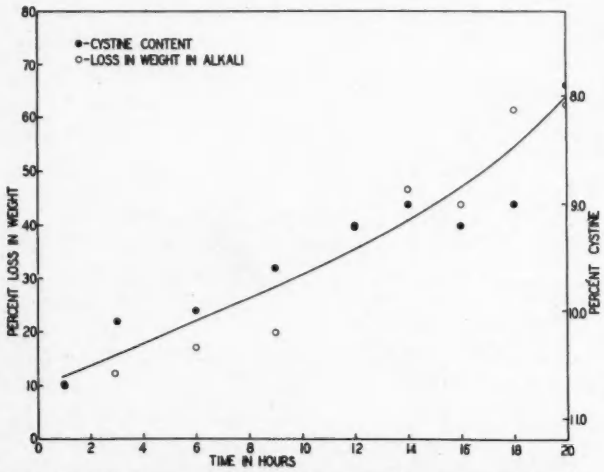


Fig. 2—Effect on wool of 2-volume hydrogen peroxide solutions at 50° C. for different lengths of time.

loss in weight in alkali increases with increasing time of treatment, there does not appear to be any critical time under the conditions of these experiments.

4. Effect of Varying the pH of the Hydrogen Peroxide Solutions

Samples of wool yarn were treated with 2-volume hydrogen peroxide solutions, differing in pH*, for 3 hours at 50° C. and then analyzed for cystine content and alkali-solubility. The results, shown in Figure 3, indicate that pH has no appreciable effect on the oxidation of wool by peroxide below about pH 7. Between pH 7 and pH 10 the alkali-solubility increases and the cystine content decreases with increase in pH. Above pH 10 the cystine content continued to decrease but the alkali-solubility also decreases. This is due to the fact that above pH 10 the alkali concentration in the hydrogen peroxide bath becomes sufficiently high to dissolve a portion of the wool

*The buffers were prepared according to Clark[12] and were approximately M/50 with respect to salt.

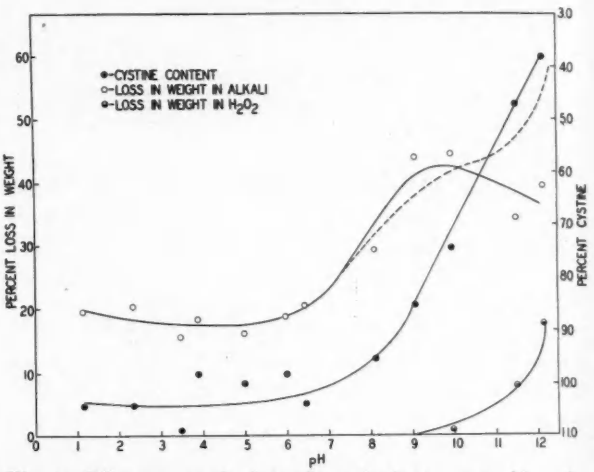


Fig. 3—Effect on wool of 2-volume hydrogen peroxide solutions of varying pH at 50° C. for 3 hours. The dotted curve represents the sum of the losses in weight in the hydrogen peroxide and alkali treatment.

that would ordinarily be removed in the subsequent alkali treatment. When the loss in weight in the peroxide treatment is added to the loss in weight in the alkali treatment, the total loss in weight (as shown by the dotted curve in Figure 3) is in better agreement with the decrease in cystine content.

IV. CONCLUSIONS

Wool which has been oxidized by hydrogen peroxide solutions has a lower cystine content and a higher alkali-solubility than untreated wool. The extent to which the wool is oxidized bears a functional relationship to the decrease in cystine content and to the increase in alkali-solubility. In general, the latter may be considered to be the better measure of the oxidation. This is due to the fact, that although the main point of attack during oxidation is the disulfide group, there is evidence† indicating that other groups may be attacked which may affect the alkali-solubility but not the cystine content of the wool.

The extent to which wool is oxidized by hydrogen peroxide solutions depends on the concentration, temperature, and pH of the solutions and on the duration of treatment. The data obtained under the conditions of these experiments indicate critical values for the concentration, temperature, and pH of the hydrogen peroxide solutions, but not for the duration of treatment.

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†Investigation now in progress.

Proceedings of the American Association of Textile Chemists and Colorists

The Oxidation of Wool

The Lead Acetate Test for Hydrogen Peroxide-Bleached Wool

By ARTHUR SMITH and MILTON HARRIS†

The lead acetate test for distinguishing between untreated wool and wool bleached with hydrogen peroxide has been investigated. The degree of darkening of the wool during lead acetate treatments is a function of pH, the maximum difference between untreated and bleached wool occurring at pH 5. The results indicate that hydrogen peroxide partially oxidizes the sulfur in wool and prevents the formation of lead sulfide. A mechanism by which lead sulfide is formed in untreated wool is described.

I. INTRODUCTION

PREVIOUS work[1, 2] has shown that in the action of hydrogen peroxide on wool, the disulfied group of the cystine is oxidized and the susceptibility of the wool to deterioration during alkaline treatment is greatly increased. The extent to which the wool is oxidized bears a functional relationship to the decrease in the cystine content and to the increase in the alkali-solubility of the wool. While determinations of the cystine content or alkali-solubility of wool offer good, quantitative methods for the control of hydrogen peroxide bleaching, there is a definite need for a qualitative test for distinguishing between unbleached and hydrogen peroxide-bleached wool. Tests on the physical properties have been shown to be useless for this purpose[1]. Various dyeing tests[3, 4, 5] have been used but with only partial success since they were designed to measure damage to wool in general and lack specificity.

It is well known that under suitable conditions wool will darken when treated with solutions of lead acetate or nitrate[6, 7, 8]. More recently, this treatment has been used by Beutel and Kutzelnigg[9] to distinguish between unbleached and bleached horn and wool. Presumably, the bleached materials remain unchanged whereas the unbleached materials are darkened by the treatment. They also found that irradiated wool was readily darkened by the lead salts but that the same wool after oxidation did not give the reaction. The method they have outlined is unsatisfactory since it fails in the presence of small amounts of acid or alkali. For example, unbleached wool containing a little acid is not darkened, while bleached wool in alkaline solution is darkened by lead acetate.

The present investigation was undertaken to study the effect of pH on darkening of wool in lead acetate solutions and to determine the optimum pH for distinguishing between unbleached and hydrogen peroxide-bleached wool by the lead acetate test.

*This is the second paper of a series on studies on the oxidation of wool.

†Research Associates from the American Association of Textile Chemists and Colorists at the National Bureau of Standards.

II. MATERIALS AND METHODS

The material used for these experiments was worsted cloth, plain weave, weighing about 5 ounces per square yard, mill processed ready for dyeing. It was purified by 8 hours extraction in a Soxhlet apparatus with alcohol after which it was soaked in water at 140° F. for 1 hour. The cloth was air-dried and cut into specimens 17.5 centimeters square.

The bleached wool was prepared from the purified worsted cloth described above by treating for 1 hour at 120° F. with a solution of 2-volume hydrogen peroxide at pH 9.5, centrifuging to remove excess solution, and drying for 1 hour at 140° F. The cloth was then washed free of hydrogen peroxide and air-dried.

The alkali-treated wool was prepared from the purified worsted cloth by treating 15 minutes at 130° F. in 0.5 percent solution of sodium carbonate. This cloth was immediately washed free of alkali and air-dried.

Approximately 5 grams of the material to be tested was boiled for 40 minutes in 400 ml. of 0.05 percent solution of lead acetate of known pH, rinsed and dried at room temperature. The reflectance of the tested sample was measured with a Martens photometer[10].

III. RESULTS AND DISCUSSION

Preliminary spectrophotometric measurements at seven wave length from 405 to 703 millimicrons of the untreated and of the bleached cloth before and after lead acetate treatments were made. The results obtained indicated that measurements at wave lengths approximately 650 millimicrons would give a satisfactory measure of the darkening produced by the lead acetate test.

Samples of the untreated and of the bleached cloth were tested with lead acetate solutions varying in pH from 1 to 11, the pH of the solutions being obtained by suitable additions of hydrochloric acid or sodium hydroxide. The color of the untreated and bleached cloths tested at pH 1 was the same. The untreated cloth began to darken at about pH 2 and the bleached at about pH 3.5. Between these pH's and pH 11, the samples became darker with increasing pH. In this range the bleached samples were

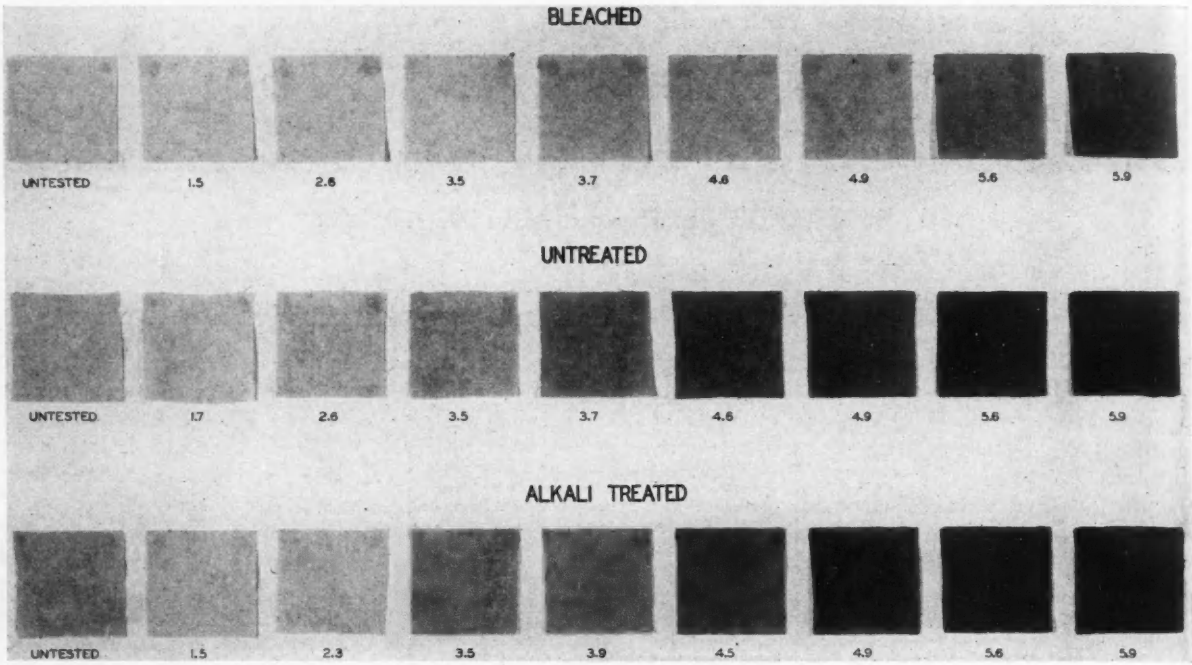

Fig. 1—Appearance of the bleached, untreated and alkali-treated wool after being boiled for 40 minutes in 0.05 per cent lead acetate solutions of varying pH.

lighter in color than the untreated, the maximum differences occurring between pH 4 and pH 5.5. At pH 11, the color of the two materials became approximately the same.

In order to obtain a more definite maximum and to eliminate the difficulties of regulating the pH with hydrochloric acid and sodium hydroxide solutions, lead acetate solutions, buffered with hydrochloric acid-sodium acetate mixtures were used[11]. A second series of untreated, bleached and alkali-treated samples were tested with these solutions at intervals of about 0.5 pH between about pH 1.5 and pH 6. The effect of the treatments is shown in Figures 1 and 2. A maximum difference in color and in reflectance at 650 millimicrons between the bleached samples and the untreated and alkali-treated samples was obtained at about pH5*.

The alkali-treated samples† are in general slightly darker than the untreated samples. However, the differences in reflectances between the two series of samples are of the same order of magnitude as the variations obtained in a series of like samples at a given pH. The results therefore do not warrant the use of the lead acetate test as a method for detection of alkali damage.

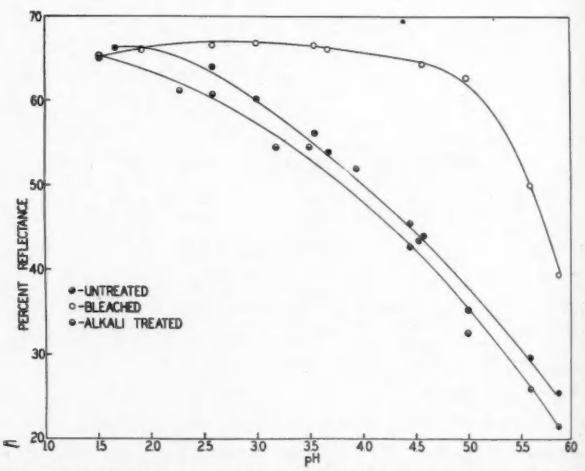

Fig. 2—Relation between the pH of the lead acetate solution and the reflectance at wave length approximately 650 m μ of the tested samples shown in Fig. 1.

In their studies on keratins, Beutel and Kutzelnigg[9] postulated that during irradiation some of the sulfur in wool was converted to sulfide sulfur which readily reacted with lead salts. Since oxidation with hydrogen peroxide prevented the formation of black lead sulfide, they assumed that the sulfide sulfur had been oxidized to sulfate sulfur. It is known that in the photochemical oxidation of wool some sulfate is formed[12] but this ac-

*Suitable buffer solutions for the lead acetate tests may be prepared according to either of the following formulas:

(I)	(II)
200 ml. 1 N sodium acetate	200 ml. 1 N sodium acetate
20 ml. 2.5 percent lead acetate	20 ml. 2.5 percent lead acetate
50 ml. 1 N hydrochloric acid	68 ml. 1 N acetic acid
730 ml. water	712 ml. water

†The alkali treatment used in this work is more severe than alkali treatments to which wool is generally exposed in practical processing.

counts for only a small portion of the total sulfur. Furthermore, Blumenthal and Clarke[13] showed that by oxidation with bromine, only about 7 percent of the sulfur in wool was convertible to sulfate. Analyses for sulfates in the bleached samples used in this work by the method of Mease[14] showed that 2.2 percent of the sulfur had been oxidized to sulfate.

Crowder and Harris[15] studied the behavior of sulfur in wool during alkali treatment and found considerable evidence that the bulk of the sulfur was present in only one form, namely, cystine sulfur. In view of this, it is improbable that oxidation of a small portion of the sulfur to sulfate would prevent the formation of lead sulfide in the lead acetate test.

Although sulfates are formed only with great difficulty by the oxidation of cystine and cysteine, there is considerable evidence[1, 2, 16, 17], that intermediate oxidation products are readily formed. The types which may be produced without splitting of the disulfide linkage are listed below:

(1) R-SO-S-R
(2) R-SO_2-S-R
(3) R-SO-SO-R
(4) R-SO_2-SO-R
(5) R-SO_2-SO_2-R

That the formation of lead sulfide in the lead acetate test is prevented by the formation of intermediate oxidation products of at least type 3 and probably types 4 and 5 was demonstrated by the following experiments*. Cystine and cystine disulfoxide (type 3) were treated with boiling lead acetate solutions at pH 5, and pH 12.5. No reactions occurred at pH5†. The cystine solution at pH 12.5 darkened in about 5 minutes and at the end of 1 hour, a heavy precipitate of lead sulfide had formed. The cystine disulfoxide solution at pH 12.5 remained clear during this time and only after prolonged boiling did a slight darkening occur.

The ease with which lead sulfide is formed on the untreated wool, especially with increasing pH, is in accord with the known lability of sulfur in wool and can be accounted for by the mechanism postulated by Crowder and Harris[15] according to the following scheme:

$$RCH_2\text{-}S\text{-}S\text{-}CH_2R \underset{\text{Decreasing pH}}{\overset{\text{Increasing pH}}{\rightleftharpoons}} RCH_2SH + RCH_2SOH$$

Increasing pH ↓↑ Decreasing pH (Increasing pH) (Decreasing pH)

$$PbS \xleftarrow{\text{Pb Salt}} H_2S + RCHO$$

The darkening of the untreated wool samples in solutions below pH 5 indicates the extreme lability of the sulfur. While acid tends to drive the equilibrium in the above equation in the direction shown by the arrows, the results indicate that some hydrogen sulfide* is formed in acid solutions to about pH 2.

*In alkaline solutions, Na_2S would be formed.
*This postulation may be made since it is known that the sulfoxides may be reduced to the sulfydryl form whereas the sulfones are not reduced under similar conditions.
†The sulfur in cystine itself is very much more stable than sulfur in cystine in the wool protein.

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MERCERIZING COMMITTEE MEETING

The meeting of the Sub-Committee on Mercerization, originally scheduled for 4 P. M. on April 18th at the Textile Engineering Hall, Alabama Polytechnic Institute, Auburn, Ala., has been postponed to April 25th at the same hour and place.

CALENDAR OF COMING EVENTS

Meeting, New York Section, Paterson, N. J., Friday, April 24, 1936.

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Council Meeting, Philadelphia, Pa., April 10, 1936.

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Meeting, Research Committee, Philadelphia, Pa., April 10, 1936.

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Meeting, Philadelphia Section, Broadwood Hotel, Philadelphia, Pa., Friday, April 10, 1936. Speakers: Ivor Griffith, Director of Research, John B. Stetson, "The Dyeing of Fur Felt"; H. D. W. Smith, Treasurer and Textile Technologist, A. M. Tenney Associates, "The Manufacture and Properties of Eastman Acetate Yarn".

* * *

Spring Meeting, Southeastern Section, Thomas Hotel, Auburn, Alabama, April 25, 1936. Speakers: Prof. Robinson, A.P.I., "Termites and Their Control"; S. M. Edelstein, A.A.T.C.C. Research Assistant, "Mercerization Research, Its Value and Practical Application"; D. H. Powers, Rohm & Haas Co., "Permanent Finishes on Textile Fabrics".

* * *

Annual Meeting, Providence, R. I., December 4 and 5, 1936.

Proceedings of the American Association of Textile Chemists and Colorists

A Test for Mercerization

in the Presence of Dyes

By SIDNEY M. EDELSTEIN*

I. INTRODUCTION AND SUMMARY

In the literature the term "mercerized cotton" has a different meaning for the theoretical Scientist than it does for the manufacturer and consumer. To the former, this term indicates cotton that has been highly swollen, whereas the manufacturer understands "mercerized cotton" to mean cotton that has been treated with strong caustic soda, usually under tension, with the result that the cotton obtains a certain amount of luster, increase in strength, dye affinity and chemical reactivity.

It is obvious that from a commercial viewpoint any term which attempts to give the "degree of mercerization" of a sample of cotton must contain an integration of the cotton's luster, strength, dye affinity, etc. Any single test for mercerized cotton can only show whether the cotton has been mercerized or not and cannot give the "degree of mercerization".

The determination of the presence of mercerization in cotton is of considerable importance however, and a number of tests for this determination have been published. These methods have proved unsatisfactory on samples of cotton containing dyes whose removal is difficult or impossible to accomplish without affecting the cotton.

The purpose of the present investigation has been to devise a test for the determination of the presence of mercerization in cotton which would not be too difficult or lengthy and which would work satisfactory on samples of cotton dyed with any type of dye.

A method for this determination meeting the above requirements has been found to be a modified form of S. M. Neale's barium hydroxide absorption method. This method is based on the fact that cotton that has been mercerized absorbs more barium hydroxide from dilute solution than does unmercerized cotton under the same conditions. The results of this test are expressed as the ratio of the barium hydroxide absorbed by the tested sample to that absorbed by unmercerized cotton under the same conditions. This ratio multiplied by one hundred is called the barium activity number of the sample.

It has been found that unmercerized cottons of different origins are characterized by a barium activity number of one hundred. Samples of commercial mercerized yarns tested by this method showed activity numbers close to 150, whereas samples of commercial mercerized piece goods showed activity numbers from 115 to 130. Further work will be necessary before an explanation can be given for the fact that the commercial mercerized piece goods gave lower barium absorption figures than the mercerized yarns.

The determination of the barium activity number of cotton, besides offering a means of determining the presence of mercerization in dyed and undyed samples of cotton should be of value in studying variations in the mercerizing process as well as furnishing a tool for further research on mercerization.

II. REVIEW OF LITERATURE

It has long been known that cotton after mercerization exhibits an increased absorptive power for iodine, dyes, moisture and alkalies, an increased reactivity towards oxidation and hydrolysis as well as a changed external and internal fiber structure. These properties have formed the basis of many tests for mercerized cotton[1, 2, 3, 4].

After mercerization, the cotton fiber has become rounded, the lumen has decreased in size and part of the convolutions of the fiber has disappeared. Hubner[5], Willows and Alexander[6] and many others have studied these changes in the microscopic appearance of cotton fibers after mercerization. Calvert and Clibbens[7] have suggested that a determination of the cotton fibers free from convolutions after mercerization can be used as a test of the mercerization process. The examination of the cotton fibers under the microscope for the determination of mercerization offers difficulties when the fibers are deeply colored.

The changes in internal fiber structure resulting from mercerization as evidenced by examination under polarized light has been studied by Harrison,[8] and as evidenced by changes in X-ray diffraction patterns by Katz and Mark,[9] Katz,[10] Andress[11] and Schramek and Shubert[12]. Preston[13] has shown that mercerized cotton has different indices of refraction than unmercerized cotton. Equipment for X-ray examination is not often available however.

Qualitative tests for mercerization based on the increased retentive power of mercerized cotton for iodine were first developed by Lange,[14] and Hubner[15] and im-

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proved by Ristenparte[16] and Ermen[17]. Schwertassek,[18] Rogovina and Mebus[19] developed quantitative methods for the determination of the presence of mercerization based on the amount of iodine retained by mercerized cotton after treatment with an aqueous solution of iodine under standard conditions. Trials of these methods showed that the presence of dyes on the samples of cotton affected the results greatly.

A number of dyeing tests for the characterization of mercerized cotton have been put forward by a number of workers[20, 21, 22, 23, 24, 25]. These tests involved comparison of unknown samples with standard samples after dyeing under definite conditions. The dyeing methods cannot be used unless any initial dye on the sample can be removed.

Schwalbe[26] first proposed the determination of the copper number of mercerized cotton after hydrolysis with sulfuric acid under standard conditions as a measure of mercerization. This method has been improved by Bernardy[27] and Abozin[28]. Birtwell, Clibbens, Geake and Ridge[29], later showed that oxidation of mercerized cotton with an alkaline hypobromite solution and the subsequent determination of the copper number possessed advantages over the Schwalbe method. Any method however involving the determination of copper numbers is too lengthy and difficult. The results are also very likely to be affected by the presence of dyes on the samples.

Vieweg[30] long ago suggested that the preferential absorption of alkali from dilute solution by mercerized cotton might be used as a measure of the mercerization of cotton.

Neale[31, 32] recently developed a method for the determination of mercerization in cotton which involves the determination of the preferential absorption of barium hydroxide from dilute solution by mercerized cotton. This writer's work (Neale) has shown that cottons of widely different origins are characterized by approximately the same degree of reactivity and that cottons mercerized in increasing strengths of caustic soda show increasing absorption of barium hydroxide up to certain limits.

III. MODIFIED BARIUM HYDROXIDE ABSORPTION METHOD

After a study of the methods mentioned above, the barium hydroxide absorption method appeared to meet the requirements of a suitable test and this method has been studied and modified in the present work. The modified procedure differs from that of Neale essentially in the fact that the absorption of a sample of unmercerized cotton treated in the same manner as the unknown sample is determined with the absorption of the latter (unknown sample) and the results are expressed as the ratio of the absorption of the tested sample to that of the standard unmercerized sample. This obviates the necessity for making certain corrections, for having the tests run at exactly the same temperature and in exactly 0.25N. barium hydroxide solution. The experimental work below shows that the absorption ratio for a definite sample of mercerized cotton is the same at different temperatures and in different concentrations of barium hydroxide solution (within limits). The kind of unmercerized cotton used as the standard does not affect the absorption ratio (Egyptian cotton may make a slight difference). Since the standard and unknown sample are dried and conditioned together, and the moisture is absorbed by both samples in a constant ratio,[33] the barium absorption ratio is unaffected by humidity variations.

Corrections for the fact that the samples are not in equilibrium with the same final solution concentration are not made as these corrections are small and remain constant for any particular range of samples.

The following modified absorption method was adopted and used throughout this work.

(1) Unknown sample and sample of grey cotton yarn are scoured, washed and dried under standard conditions at the same time. (See below for scouring procedure.)

(2) Samples are allowed to condition a short time in the room and then two grams of the samples are weighed into small flasks (200cc). Duplicates are run on each sample.

(3) 30cc of barium hydroxide solution of approximately N/4 are added to the flasks which are then stoppered and allowed to stand about two hours with frequent shaking.

(4) After two hours, 10cc of the solution in each flask are withdrawn and titrated with standardized acid, approximately N/10 using phenolpthalein as indicator. 10cc of the barium hydroxide solution (blank) are also titrated. The same pipette, burette, etc. must be used throughout on each determination.

(5) From the figures obtained above, the ratio of the amount of barium hydroxide absorbed by the unknown sample to that absorbed by plain cotton (standard) is determined. This figure is multiplied by 100 and called the barium activity number.

Example: 2 gms. of a commercial mercerized yarn and 2 gms. of unmercerized cotton (standard) gave following figures after two hours standing in 30cc. of barium hydroxide solution.

Titration made with 0.1000 N. acid.

Titration of 10cc of barium hydroxide solution (blank) equals 24.30cc.

Therefore milli-equivalents in 30cc of initial solutions equals 3.000 x 0.1000 x 24.30 equals 7.290.

Titration of 10cc of final solution containing mercerized sample equals 19.58cc.

m.e. in 30cc of final solution equals 3.000 x 0.1000 x 19.58 equals 5.874.

Therefore m.e. absorbed by mercerized sample equals 7. 290 minus 5.874 equals 1.416.

Titration of 10cc of final solution containing standard equals 21.20cc.

m.e. in 30cc of final solution equals 3.000 x 0.1000 x 21.20 equals 6.360.

Therefore m.e. absorbed by standard equals 7. 290 minus 6.360 equals 0.930.

Barium activity number of mercerized sample equals 100 x 1.416 equals 153.

$\frac{0.930}{}$

IV. MATERIALS AND METHODS

(1) Reagents.

An approximately N/10 solution of hydrochloric acid was standardized against sodium carbonate and used as the standard. The barium hydroxide solution was prepared by dilution of a filtered saturated solution with freshly distilled water and was made approximately 0.25 normal. This solution was placed in a large bottle which was connected to a 30cc delivery pipette. The air entering the system passed through a tube containing soda lime.

(2) Scouring procedure.

The following method was found to give good results for the absorption determinations.

Twenty-five grams of sample are boiled for one hour in a liter of water containing 10 gms. of soap (olive) and two grams of soda ash. The samples are then washed repeatedly in warm distilled water until free from soap and alkali, squeezed and dried in a drying oven at 212 degrees F., until thoroughly dry. If the samples contain starch, this is removed after the scouring operation by treatment with a solution containing 0.5% to 1% of a starch-liquefying enzyme for thirty minutes at 150 degrees F.

In the case of a few commercial samples which are heavily finished with mineral oils and waxes or with salts such as magnesium sulfate or zinc chloride, the soap scouring operation must be substituted by an extraction with carbon tetrachloride or other solvent followed by an hour's boil in plain water.

V. EXPERIMENTAL RESULTS

The effects of the variables of time, temperature and barium hydroxide concentration on the modified barium hydroxide absorption method were studied and the barium activity numbers of raw cottons, dyed and undyed commercial mercerized and unmercerized yarns and cloths were determined.

(Note)—In the study of the variables affecting the test the same mercerized yarn was not used for all the determinations, but the same yarn was used throughout each determination.

(1) *Effect of time on absorption.*

Sixteen grams of scoured unmercerized cotton yarn and sixteen grams of scoured commercial mercerized yarn were placed in two flasks each containing 240cc of 0.2430 normal barium hydroxide solution. 10cc portions were withdrawn from time to time for analysis. The results given in Table I show that absorption is complete after two hours standing.

TABLE I

Observed absorption (milli-equivalents per two grams cotton) from 0.2430 normal barium hydroxide solution at 77° F. (25° C.)

Time (hours)	½	1	2	3	4	5
Unmercerized cotton	0.912	0.912	0.927	0.927	0.927	0.927
Mercerized cotton	1.401	1.401	1.416	1.416	1.416	1.416

(2) *Effect of temperature on absorption and activity numbers.*

Absorption measurements made at various temperatures on unmercerized cotton yarn and a commercial mercerized yarn are shown in Table II.

The amount of barium hydroxide absorbed is greater, the lower the temperature of the determination. The activity number of the mercerized cotton remains constant over the temperature range of the experiment.

TABLE II

0.2430 N. barium hydroxide solution used.
A equals mercerized sample.
B equals unmercerized sample.

Temp.		*m.e. of hydroxide absorbed by 2 gms. of sample*	*activity number*
32 degrees F.	A	1.657	153
(0 degrees C.)	B	1.085	
61 degrees F.	A	1.490	154
(16 degrees C.)	B	0.969	
75 degrees F.	A	1.416	153
(24 degrees C.)	B	0.927	
100 degrees F.	A	1.335	153
(38 degrees C.)	B	0.868	

(3) *Effect of strength of barium hydroxide solution on absorption and activity numbers.*

Absorption determinations were made on mercerized and unmercerized yarn at different initial concentrations. The results which are shown in Table III and graphed in Figure I, show that with increasing concentrations, there is an increase in the amount of barium hydroxide absorbed, but that the activity number of the mercerized yarn remains constant over the range between 0. 1610 normal and 0.2946 normal.

(4) *Effect of various pretreatments on activity numbers.*

The activity number of samples of a commercial mercerized yarn was unaffected by the following pretreatments. (1) Regular scouring method and treatment with enzyme. (2) One hour boil in solution containing 1% sulfonated castor oil and 0.2% soda ash. (3) One hour boil in 1% pine oil and 0.2% soda ash solution. (4) Reg-

TABLE III

Determination at 77° F. (25° C.)
A equals commercial mercerized yarn.
B equals unmercerized yarn.

Initial conc. N.		*Final conc. N.*	*m.e. absorbed by 2 gms.*	*Activity No.*
0.1610	A	0.1268	1.026	155
	B	0.1389	0.663	
0.2580	A	0.2086	1.482	155
	B	0.2261	0.957	
0.2946	A	0.2394	1.656	155
	B	0.2589	1.071	
0.4474	A	0.3761	2.139	151
	B	0.4002	1.416	

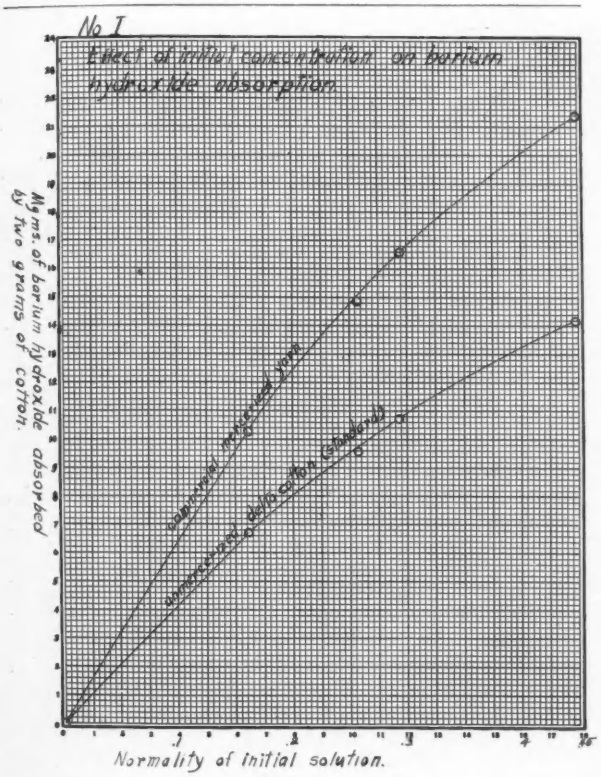
No I
Effect of initial concentration on barium hydroxide absorption
Mg.ms. of barium hydroxide absorbed by two grams of cotton.
commercial mercerized yarn
commercial delustered cotton Gassed
Normality of initial solution.

Fig. 1

ular scouring followed by treatment in dilute sulfuric acid and then washing. (5) Regular scouring but dried in laboratory room. (6) Extraction with carbon tetrachloride, alcohol and water.

This indicates that the scouring procedure can be modified to suit conditions of sample without affecting the results.

(5) *Activity numbers of raw cottons.*

The activity numbers of a wide variety of raw cottons were determined using a 1 7/32 inch Miss. Delta cotton as the standard. The cotton samples were all cleaned thoroughly by hand and scoured with the standard procedure. All the cottons tested showed the same activity number with the exception of a sample of Egyptian Sak. cotton. The latter had a slightly higher number than the rest. See Table IV.

TABLE IV

Activity numbers of raw cottons cleaned by hand.

Cotton	*Activity Number*
1 7/32 in Miss. Delta	100
1 5/32 in. Miss. Delta	100
1 inch Georgia	100
1 inch Louisiana	100
1 inch Texas	100
1½ inch Egyptian Sak.	103

(6) *Effect of dyes on activity numbers.*

The activity numbers of mercerized and unmercerized regardless of the presence or kind of dyes on the samples. yarns dyed with a variety of dyes were determined. The unmercerized samples showed an activity number of 100 The mercerized samples also showed practically the same activity number throughout. Results for the mercerized samples are shown in Table V.

TABLE V

Activity numbers of a commercial mercerized yarn dyed with the following dyes. Dyes were not stripped from samples.

Kind of dye	*Activity Number*
vat purple	144
sulfur blue	146
vat blue	145
aftertreated direct brown	145
napthol red	145
sulfur grey	146
vat yellow	145
direct brown	146
plain gassed undyed	147
plain undyed	147

(mercerized yarn dyed with crystal violet on tannin-tartar-emetic mordant equaled 151. Same yarn before dyeing equaled 150).

(7) *Activity numbers of various commercial samples of cotton cloth.*

A wide variety of commercial mercerized and unmercerized samples of cloth were tested. All samples of mercerized cloth tested gave lower activity numbers than samples of mercerized yarn. See Table VI.

(8) *Presence of fibers other than cotton.*

Regenerated rayons gave activity figures between 250 and 270. These figures are much higher than for mercerized cotton. Acetate rayon, wool and silk react with the barium hydroxide solution and should not be present in absorption determinations.

VI. CONCLUSIONS

The above work shows that the modified barium hydroxide absorption method is suitable for determining

TABLE VI

Activity numbers of commercial cloth samples.

Unmercerized

Sample	*Activity Number*
grey 64 by 60 5.35	101
bleached 64 by 60 5.35	100
bleached broadcloth	100
direct yellow 64 by 60 5.35	100
sulfur navy 64 by 60 5.35	100
vat 80 by 60 5.00	99
bleached 128 by 68 4.10	100
grey 48 by 40 5.50	100
grey 195 Twill	100
grey 236 Twill	100
grey 210 Twill	100
grey 190 Twill	100
grey 250 Drill	100
vat khaki 250 Drill	100
sul. khaki 190 Twill	100
sul. black 195 Twill	101
sul. navy 195 Twill	100

Mercerized

Sample	*Activity Number*
bleached broadcloth	130
vat yellow broadcloth	130
vat yellow 48 by 48 4.00	127
vat blue 48 by 48 4.00	127
bleached 88 by 80	130
sul. brown 235 Twill	130
sul. navy 235 Twill	130
vat blue 235 Twill	125
vat khaki 195 Twill	118
vat tan 195 Twill	116
vat yellow 236 Twill	116

whether a sample of cotton has been mercerized and that it also offers an indication of the activity of the mercerized cotton. The determination is easy to carry out and the physical form of the samples or the presence of dyes on the samples do not interfere with the test. The variables of temperature, barium hydroxide concentration and time of standing (above two hours) do not affect the results of the test.

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Proceedings of the American Association of Textile Chemists and Colorists

Stainless Steel

in the Textile Industry*

By GEORGE W. HINKLE†

CORROSION of ferrous metals by the atmosphere, water and various conditions required in industrial operations is very costly. Sir Robert A. Hatfield, a famous British metallurgist, made the statement in 1922 that the loss by rust and corrosion of ferrous metals was probably no less than $3,000,000,000. He amended this statement in 1933 in the London "Times" when he suggested "the loss due to wastage in 1932 alone was 67,000,000 tons", which amount is about 19,000,000 tons in excess of actual iron and steel production for that year.

A number of non-ferrous metals which possess greater corrosion resisting qualities than iron or steel have been applied in many forms to combat this serious corrosion loss. In a large number of cases these metals, while superior to iron, have not been entirely satisfactory, either because of economics, physical characteristics of the metals or contamination of the products being processed. This latter is very vital to the chemical, textile, food and allied industries where purity and freedom from contamination is of prime importance.

It has been in these industries that stainless steel has received its greatest acceptance due to its inherent ability to withstand corrosion and attack by a great number of chemicals. The nitric acid industry alone applies tons of this metal annually to equipment.

Stainless steel is a relatively new metal, discovered during the period of 1912-1914 when both Germany and England were conducting investigations on alloys for ordinance and heat resisting equipment. They were used to a limited degree during the war but were not actively manufactured in Europe until 1922 and in this country until 1925.

The introduction of stainless steel to industry was slow. The prospective user had to be convinced that the metal offered advantages superior to his present materials. Time was required for special tests and experimental work. The machine and equipment builder must learn the fabricating characteristics of the metal. Sometimes new equipment was needed to properly work stainless steel, for it is tougher and nearly twice as strong as ordinary steel and many times as strong as copper and aluminum.

This period is past, fabricators have placed themselves in a position to produce high quality machines and equipment. The steel manufacture has eliminated some of the early defects which are always encountered in new developments and today we refer to our product as "ENDURO", the perfected Stainless Steel, which we sincerely believe it to be. At present there are approximately 50 commercial alloys designated as Stainless Steels. They all possess different physical, mechanical and corrosion resistant properties for special applications. These however, may be classified for general purposes into two groups.

(1) Straight Chromium Alloys. 12-30% Chromium.

(2) Chromium nickel alloys. 18% Chromium—8% Nickel. With or without additional elements as desired.

The corrosion resistance of these alloys is attributed to the chromium content. Theoretically, the chromium develops an invisible chromium oxide film on the surface of the metal. This film is impervious to penetration by atmosphere and a great number of chemicals. Nickel and also molybdenum when added to the chromium alloys increase the effectiveness of this film.

The first group is magnetic, fairly ductile but does not lend itself satisfactorily to welding unless heat treated after welding. The second group is non magnetic, superior in corrosion resistance and ductility and produces excellent welds. The welds are equal to the base metal in ductility strength and corrosion resistance and require no subsequent treatment other than removing scale formed in welding.

You are all familiar with the hazards presented to the dyer and finisher by the use of metal equipment. The acid and bleach solutions used in processing, not only have corroded the metal to a degree requiring constant replacement, but in a number of cases have reacted with the solutions either as a catalyst or directly, thus producing corrosive products or chemical changes in the solutions. This results in rejections and reprocessing of the fabrics.

Because of this dissatisfaction with metal, considerable wooden equipment is in use at the present time for dye tubs and bleaching tanks. However, the color retention of wooden tubs necessitates boil outs and washings resulting in low production rates and high costs. Bleaching solutions deteriorate the wood at excessive rates and the splintering frequently results in torn fabrics.

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†Republic Steel Corp.

Aware of these factors in the industry The Republic Steel Corporation in conjunction with the Philadelphia Textile School conducted a number of tests to determine where these alloys could be successfully used and to what advantage. The results of this investigation were presented before your Philadelphia Section last year and I will not explain in detail data resulting from this work. We have copies of this report here tonight for your reference.

The general outline of this work consisted of determining the effect of the various solutions on the metal, such as corrosion and film formation and also the effect of the metal on the solutions. This entailed a number of corrosion tests where corrosion was determined as loss in weight of metal and a series of dye tests in which metal effect was observed as change in color.

The results of this work indicate that two types of Stainless Steel alloys are ideally suitable for handling textile dye and bleach solutions. Enduro 18-8-S which is an 18% chromium 8% nickel alloy with .08 max carbon and Enduro 18-8-S Mo with practically the same chromium, nickel and carbon contents and 2-4% addition of molybdenum.

The addition of molybdenum as previously mentioned increases the effectiveness of the chrome oxide film, making it more resistant to the stronger reducing acids, such as sulfuric, acetic and formic. This alloy we found to be more suitable for wool dyeing and acetic acid ageing where these acids are used in fairly high concentrations and at boiling temperatures. This alloy does not effect the color of either the acid or acid chrome dyes when subjected to these solutions for 18 hours. We tested over 50 dyes picked at random and while stainless had no affect on these colors only 12 were not effected by a copper nickel alloy which has been used extensively, being the most satisfactory metal available up to this time. Since the completion of these tests a well known dyestuff manufacturer has duplicated these findings on its most sensitive chrome dyestuffs.

The tests also indicated that the chrome nickel alloys without molybdenum are entirely satisfactory for cotton bleaching and dyeing operations.

This alloy is suitable for cotton dyeing and has no effect on direct, vats, sulfur or diazotized and developed colors. The sulfur colors do not produce the dark discoloration of metallic sulfides on stainless steel as are so common on copper and copper nickel alloys. The nitrous acid of the diazotizing bath does not attack the alloy or effect the color. Incidentally, one eastern dyer who is doing considerable vat dyeing on materials for rubberizing, has changed 100% to Stainless Steel to eliminate the possible absorption of copper by the fabric which is claimed to be detrimental to the fabric in subsequent rubberizing.

Bleaching

Stainless Steel can be used satisfactorily with bleaching solutions. Tests have been conducted in hypochlorites, peroxides, permanganates and sulfur dioxide and the steel has been found to be resistant to these solutions. Preliminary tests have indicated that they do not produce a catalytic action on the rate of the decomposition of the solutions which might result in tendering or over oxidation of the fabrics. However, we do not like to recommend this metal for standing solutions of hypochlorites. Although some tests, both service and laboratory indicate it to be satisfactory.

Stripping Baths

Stainless Steel is resistant to the hydrosulfite stripping baths used in finishing and processing. The metal is not attacked or discolored. Hence it offers a clean surface for subsequent operations.

Ageing

Stainless has also been found satisfactory for acetic and sulfite ageing equipment. However, before making applications of this type we suggest test installations as we have found quite a variance in corrosive conditions on ageing equipment in a number of plants. The chrome nickel molybdenum alloy is more suitable for these installations.

Stainless steel can be used economically for processes other than described above, such as singe rolls, sizing equipment, slasher rolls, bleaching Kiers and Kier equipment. It is not only inert to chemical solution but its physical characteristics suggest a wide range of usefulness. It has high strength values and ductility for fabrication. Its surface is hard and more resistant to wear and abrasion. This greater strength permits the use of lighter gauge sections in constructing self supporting equipment, such as tanks, Kiers, dye sticks and racks where its greater resistance to denting and scratching prove beneficial.

At the present time we feel Stainless Steel is the most economical and satisfactory metal for wet processing equipment. In concluding, I wish to thank the Piedmont Section of the A. A. T. C. C. on behalf of the Republic Steel Corporation for permitting this discussion and presentation of our film.

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WET PROCESSING and the Knitting Arts Exhibition

IT has been brought to our attention that an erroneous impression is current among some wet processors of hosiery and other knit goods as regards the scope of the Knitting Art Exhibition held in Philadelphia each year. It becomes apparent that a few of the dyers and chemists engaged in the wet processing of knit goods are of the opinion that this exhibition holds no particular interest for them. To those who have attended the exhibition in the past we need not explain that there are many exhibits that appeal directly to the above mentioned persons but in view of the fact that there are some who may be unaware of what is displayed we feel we should bring the facts to their attention. Considerable space each year is devoted to displays of dyeing and finishing machinery, laboratory apparatus, chemicals and finishing specialties—all of which are of extreme importance to the well informed dyer or chemist.

We do not wish to create the impression that the rest of the exhibits are of no interest at all to the wet processing branch of the knit goods field. However, we do think it important to call to the attention of those of our readers who have not attended this exposition before that there are exhibits especially planned for their benefit. On another page in this issue we have listed a number of exhibitors whose displays we think have a special attraction for the readers of this journal. We believe it will be well worth your while to attend the exhibition on one of the days it is being held this year and see, hear and learn. The AMERICAN DYESTUFF REPORTER will have a booth and representatives of the editorial and business staffs will be in attendance to offer whatever information you may desire regarding any or all displays. There is no doubt but what this exhibition has proven of value to every dyer, finisher and chemist who has an interest in the knit goods industry.

In keeping with the occasion we shall have a number of special articles in our issue of April 20th dealing particularly with the equipment and methods of dyeing and finishing knit goods. We urge you to make every possible effort to be present at least one day during the week of April 20th. As we indicated in our last issue the exhibition this year will be considerably larger than the one held last year and you will surely be amply repaid if you attend.

MORRIS R. POUCHER

MORRIS R. POUCHER, who will long be remembered for his work on behalf of the American chemical industry, died suddenly on February 11th when stricken with a heart attack. At the time of his death he was connected with the American Fuels Corp, an affiliated company of the American Cyanamid Corp.

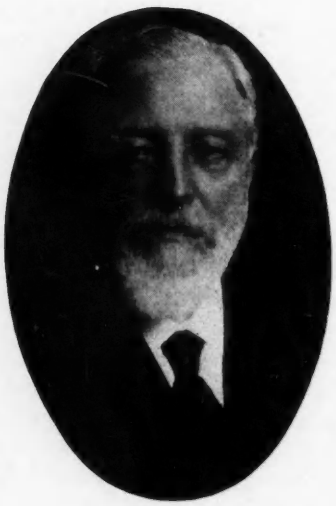
Mr. Poucher was for many years chief representative of the largest of the German dye corporations but upon the occasion of the sinking of the Lusitania he immediately resigned this position and devoted his energy and valuable knowledge of the dyestuff business to the building of an American dyestuff industry to free this country from dependence on foreign sources. In 1916 he joined E. I. du Pont de Nemours & Company and was instrumental in the erection and operation of their first dye manufacturing plant. He later became sales manager of dyestuffs for this company. At the conclusion of the war he became associated with Francis P. Garvan and Charles H. Herty in a determined effort to secure legislation which would permit the new industry to continue on a firm foundation. Their long and arduous labors were eventually fruitful and victory was theirs.

In December, 1934, Mr. Poucher, Mr. Garvan and Dr. Herty were tendered a testimonial dinner by the Synthetic Organic Chemical Manufacturers Association, of which organization he was a charter member, in recognition of their services on behalf of the American Chemical industry. At this time he was made an honorary member of the Association. At the regular meeting of this organization in February, a resolution was adopted taking recognition of his enthusiasm and uninterrupted labors on behalf of the chemical industry of the United States.

Mr. Poucher was 76 at the time of his death and resided in Scarsdale, N. Y. He is survived by his widow, two daughters and a son.

ADOLPH KUTTROFF

ADOLPH KUTTROFF, a director of the General Dyestuff Corp., died on March 23 at his home in New York City. Mr. Kuttroff, a pioneer in the dyestuff industry, was born on May 23, 1846, in Suiz, Wuerttemberg, Germany, and came to the United States in 1860.



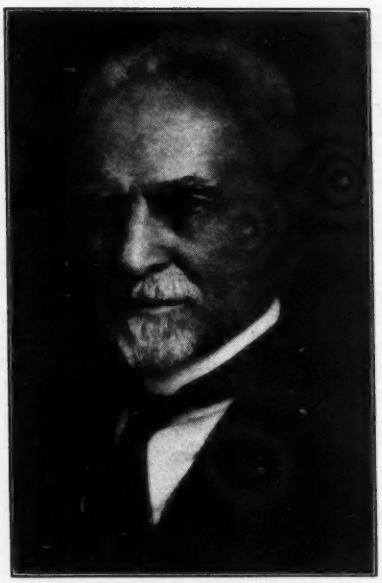
Upon his arrival in this country he became associated with the business of Adolphus Keppelman, an importer of dyestuffs and textiles and was made American agent for A. Poirrier of Paris, one of the prominent French dyestuff manufacturers of that time. The following year he founded, with William Pickhardt, the firm of Pickhardt & Kuttroff which represented the French concern until 1876. They also represented the Badische Anilin and Soda Fabrik of Ludwigshafen, Germany. When Mr. Pickhardt died in 1894 the firm continued under the same name until 1899. In 1900 Karl Pickhardt, a brother, joined the concern and it was incorporated. In 1906 the name was changed to Continental Color and Chemical Company which was dissolved the following year and became known as the Badenese Company of New York with Mr. Kuttroff as president. Liquidation of this firm took place in 1917 but the heads of the business continued operations under the name of Kuttroff, Pickhardt & Co. When the General Dyestuff Corp. was founded in 1925, Mr. Kuttroff acted as chairman of the board of directors. He retired from business in the following year but remained a member of the board.

Mr. Kuttroff will be remembered as the first importer of synthetic dyestuffs which at the time were comparatively unknown in this country.

He was one of the oldest members of the German Society of New York, belonging to this association since 1875. He was also active in the affairs of the Isabella Home, Lenox Hill Hospital, Liederkranz and German Press Clubs, the former German Savings Bank and the Guardian Life Insurance Co. His wife died in 1904. He is survived by his sons, Edwin, Arthur and Percy, and three daughters.

GEORGE A. PROCHAZKA

DR. GEORGE A. PROCHAZKA, who was active in the development of the dye industry in this country, died at his home in East Orange, N. J., on March 24th. He was 80 years old. He was born in Milwaukee and educated in private schools in New York City and studied chemistry in Germany, taking the degree of Doctor of Philosophy at Heidelberg.



Upon his return to this country he spent some time at Stevens Institute and later became a partner in a firm of consulting and analytical chemists. Still later he was chemist for the Tartar Chemical Co. and in 1893 he became associated with the Heller & Merz Co. He did much to develop the production of coal tar dyes for this company during the early eighties and until 1897 when he formed with his brother, the late John Prochazka, the Central Dyestuff and Chemical Co. in Newark. During the World War this company developed the manufacture of basic raw materials which had been previously imported. He also assisted the Federal government with legislation designed to develop the dye industry of this country.

Dr. Prochazka was a member of the American Institute of Chemical Engineers and the American Chemical Society. He is survived by his widow, two sons, George A., Jr., and J. Albert, and a daughter.

WILLIAM A. HAMANN

WILLIAM A. HAMANN, retired chemist whose home was in Mount Vernon, N. Y., died at Miami Beach, Fla., on March 24th. He was 75 years old and died in a hospital where he had undergone an operation. He was born in Hoboken, N. J., and attended Hoboken Academy.

He entered the employ of Fritzsche Bros. in 1875 and in 1884 he was New York agent for the Seely Manufacturing Co. of Detroit and Lloyd Bros. of Cincinnati. In 1885 he became associated with the Roessler & Hasslacher Chemical Co. and in time held in succession the positions of secretary, treasurer, first vice-president, president and chairman of the board of this company.

He was a member of the Drug and Chemical Club of New York, New York Athletic Club, Siwanoy Country Club and Winged Foot Country Club. He is survived by his widow; four sons, Adolph M., William A., Jr., Carl F. and Edmund H. and two daughters.

Technical Notes—

(*Continued from page* 172)

The previous section dealt fairly fully with the distinctions between the various kinds of starches. The present section deals with the methods of preparation of the soluble starches.

A considerable number of patents covers the subject up to the present. From the practical standpoint, the methods of preparation can be divided into those which are suited for the "opening up" of the starch (common) in the finishing plant itself (i.e., "home-cooking processes"), and those which require special equipment of very careful control, and so find their use in those plants which produce the soluble starches in large and regular quantity, for sale. Of the methods in use, we may distinguish the following general procedures:—

(1)—Heating with water under pressure,
(2)—Action of acids,
(3)—Action of alkalies,
(4)—Action of oxidizing agents, and
(5)—Enzymatic action.

Even through pasting up at the ordinary temperature, and drying the paste formed, common starches are converted, to some extent, into products which swell in the cold. Kantorowicz, for example (German Patent No. 250,405), stirs up the starch with water to a paste, dries it down again upon heated cylinders, and grinds up the flakes. German Patents Nos. 390,178 of V. Stein, and 401,361 of A.-G. fuer chem. Produkte vorm. Scheidemandel are similar. For opening up the starch according to such procedures, heating under pressure is very suitable.

The most important method for producing soluble starches, however, seems to be that of allowing acids to act upon the raw starches. On the small scale, at least, this method is one of the most satisfactory. A laboratory method has been given by Lindner, which prescribes covering the best quality of potato starch with 7.5 per cent HCl, and allowing to stand for three days, when the mixture is filtered, washed, neutralized, and dried. Such procedures vary in the factors of quantity of starch, temperature, and length of reaction; e.g., Gore employs, for one part of potato starch, 1.5 parts of HCl of 13 per cent, and allows to stand for six days at the ordinary temperature, the final yield being 75 per cent.

On the large scale, the methods generally used follow these laboratory procedures. For example, the starch is treated with dilute mineral acid at 40°-50° C., the proportions being so adjusted, for the temperature, that the reaction is complete in at least twenty hours. The decrease in viscosity is followed up constantly, and the mixture is rapidly neutralized when the desired viscosity has been reached. The starch is then washed in rotating filters, dried, and sifted through fine-meshed sieves. Oxalic acid is also recommended in the place of mineral acids, though Sieber states that even with small amounts of acid an undesirable hydrolysis to sugars takes place.

Alkalies have also been recommended for the purpose; e.g., Depierre recommends 76 parts of water, 16 parts of potato starch, and 8 parts of caustic soda solution of 25° B. The process has not been taken up technically, as the paste becomes extremely viscous, and does not allow the working up of much starch at a time. Recently, however, several patents have followed up the method, modified by use of non-aqueous media with aqueous caustic soda; but there is little information available as to how far such methods have actually been put into practice.

As to oxidizing agents, activin and certain per-salts have gained some favor. Even sodium hypochlorite has been recommended. Still other means have been studied along lines similar to the methods above indicated; but the above seem to be those only which are worth definite mention.

Printing of Basic Dyestuffs

German Patent No. 497,548 (*May* 13, 1930)—*I. G. Farben-Ind. A.-G.*—The point of the procedure here protected consists in the addition to the printing paste of organic compounds containing sulfur, as fixing agents; and also in the addition of organic solvents, and in some cases also neutralizing agents, with or without reducing agents. The substance containing sulfur may in some cases serve as the organic solvent also. As these solvents are specified "glycerol acetate," glycol esters, and ethylene thio-diglycol. As neutralizing agents are mentioned caustic alkalies, and the salts of these with weak acids, as sodium or potassium carbonates, sodium acetate, etc.

The method is claimed to give better results than the use of tannin-antimony mordants—the results are faster and cheaper to attain.

Vat Dyestuffs and Intermediates (Pyranthrone Series)

German Patent No. 491,425 (*February* 10, 1930)—*I. G. Farben-Ind. A.-G.*—The products whose preparation is protected by the specifications of this patent are highly halogenated pyranthrones, containing more than four halogen substituent atoms, of the same or different nature.

Pyranthrone or its derivatives, including those halogen derivatives which contain from one to four halogen substituent atoms, are subjected to intense and exhaustive halogenation in any manner in which intense halogenation is customarily carried out; for example, by the direct action of halogen in chlorsulfonic acid as a medium, and in the presence of one or more catalysts, or carriers, which may be used singly, in mixture, or successively.

For example, pyranthrone itself may be brominated in chlorsulfonic acid as a medium, without use of pressure, at temperatures below 100° C.; under some conditions chlorine will also enter (from the catalyst, for example). It is possible to cause even eight atoms of halogen, the same or different, to enter, a lower number or even a still higher number of halogen atoms being also capable of introduction.

As the pyranthrone molecule is decidedly stable, the successive halogens can be forced into the molecule in a rather definite manner. By starting with already partially halogenated derivatives, other halogen atoms, of the same or different kinds, may be introduced, thus making possible various isomers for the same numerical degree of halogenation. The yields are excellent, the products are claimed to be pure (though this statement may be received with some hesitation, from the purely chemical, not tinctorial, viewpoint).

The products are either already vat dyestuffs of great fastness, or are at least very promising as intermediates for further working up.

Three examples are given.

Vat Dyestuffs (Pyranthrone Series)

German Patent No. 497,824 (*May* 14, 1930)—*Gesells. f. chem. Ind. in Basel.*—The sequence of operations here specified consists in treating pyranthrone with sulfonating agents, subjecting the products to the action of caustic alkali in the heat, and treating the products of this reaction with alkylating or aralkylating agents.

The sulfonating agent may be conc. sulfuric acid, oleum of various strengths, chlorsulfonic acid, etc. The products at this stage are genuine sulfonic acids, whose alkali salts are crystalline powders of orange color, soluble in water with the same color. When fused with caustic alkali, they pass to substances which presumably have exchanged the sulfonic for the hydroxyl group (whatever else may also have taken place elsewhere in the nucleus). They act as vat dyestuffs, of great color-strength, but the dyeings are not fast to acid. By alkylation or aralkylation, the color of the products becomes very fast.

The products are chemically homogeneous in the technical sense, and upon purification do not particularly alter in tone.

One example is given.

Brown Vat Dyestuffs (Anthanthrone Series)

German Patent No. 493,409 (*March* 7, 1930)—*I. G. Farben-Ind. A.-G.*—The present process consists in reacting together halogenated anthanthrones with 1-amino-anthraquinone-2-aldehyde; an elevated temperature, neutralizing agents, and catalysts are employed, in suitable high-boiling solvents or media.

Thus, 3.85 parts of brom-anthanthrone (see G. P. No. 478,738) and 2.5 parts of 1-amino-anthraquinone-2-aldehyde are mixed with 100 parts of nitrobenzene, 2 parts of anhydrous sodium acetate and a little copper powder or suitable copper salt added, and the mixture boiled under stirring for several hours. On cooling, the product, which will have separated out largely, is filtered off, washed with alcohol, water, and dilute nitrate acid, then with water, to remove inorganic compounds, and dried. It forms a brown crystalline powder, soluble in conc. sulfuric acid with a green color, which has a weak reddish tinge by transmitted light, dissolves in hot nitrobenzene or trichlorbenzene with a brownish-yellow color, and crystallizes from these solvents, on cooling, in brown, rod-like crystals, often stellately grouped. Its hydrosulfite vat is reddish-violet; cotton is dyed from it the same color, which on soaping goes over to the permanent tone of bright reddish-yellow-brown, of very good fastness.

Four examples in all are given.

Azo Dyestuffs, Developed (Naphthol AS Series)

German Patent No. 494,414 (*March* 26, 1930)—(*addition to G. P. No.* 422,467 *of April* 12, 1924)—*L. Cassella and Co.*—The principal patent protected the discovery that the azoxy- or azo-derivatives of the 2-hydroxy-3-naphthoic anilides possess so decided an affinity for vegetable fibers, that they are able to dye cotton directly, after the manner of the direct cotton dyestuffs, and that they are not removed from the fiber by washing.

The present patent extends the general scope of the original patent, to cover those arylamides or diarylamides of 2-hydroxy-3-naphthoic acid, which contain in the arylamido nucleus the thiazole or triazole grouping, at least once. Exception is made of the arylides from 2-hydroxy-3-naphthoic acid and amino-naphthol-sulfonic acids, the latter of which contain a benzothiazole group. The arylides of the type mentioned are padded upon cotton as usual, and developed with diazo-salts as usual. The dyeings are distinguished by a special brilliance of tone, as well as by excellent fastness-properties.

Several examples are given.

Waterproofing—

(*Continued from page* 169)

leatherette cloths decomposed by traces of both copper and manganese, whose main source is barytes used in the proofings. These showed the typical sticky stage of decomposition due to metals.

In a few unusual cases an abnormal amount of copper has been found without appreciable perishing of the proofing. The reason for this is obscure. An interesting example of damage is one in which the edges of a ground sheet became decomposed. The reason for this is that the sheet had been used with a green tent, proofed with "Willesden Green," which is a copper proofing. The flaps of the tent had been tucked under the edge of the sheet to stop drafts, and the damp grass had caused some of the copper salts to dissolve and attack the proofing.

In sulfur black and other dark-dyed mackintoshes, a form of damage is produced in the shape of white patches on the cloth surface. This is due to soluble salts remaining in the dyed cloth and being dissolved by rain so as to concentrate and crystallize them locally. Soaking the garment in water is a means of removing the trouble. This fault is akin to that found on dark hat-bands where salts crystallize and form greyish markings.

New Products—Trade Notes

• DUPONT RELEASES

Several recent additions to established lines of colors are announced by the Dyestuffs Division of E. I. Du Pont de Nemours & Company.

"Diagen" Orange MG (Patented)—a new addition to the division's line of stabilized azoic colors for use in printing cotton. It produces bright, yellow shades of orange said to be of good fastness to washing at 160°F. and to power laundering with chlorine and of satisfactory resistance to light. This new product is used in self shades as well as in combinations for the production of browns. Like the rest of this class of colors, "Diagen" Orange MG is easy to apply and develops rapidly.

"Acele" Scarlet B—recently added to the line of acetate fiber colors, yields yellow shades of red on both bright and delustered acetate fiber yarn and piece-goods. It is said to penetrate well and to exhibit very good general dyeing properties. The fastness of this dye to bleaching, rubbing, hot pressing, scrooping and steaming is said to be very good. Furthermore, it is said to possess good resistance to light and washing at 120°F. "Acele" Scarlet B finds use in dyeing women's dress-goods and similar materials, in both straight and combination shades, being particularly recommended by the manufacturers for discharge prints because of its good discharging properties.

"Celanthrene" Navy Blue BP Concentrated—a new offering for use on acetate fiber materials giving full shades of navy of a reddish tone. The fastness and application properties of this dyestuff are claimed to be good. For this reason and because of its desirable shade, it finds use in producing navy blues on dress-goods, draperies and decorative fabrics.

"Sulfanthrene" Pink FFC Paste, "Sulfanthrene" Blue 2BDC Extra Paste, and *"Ponsol" Jade Green Supra C Paste*—three new types added to the line of vat colors for printing on delustered rayon. They produce respectively, pink, medium blue, and bright, bluish green prints said to be of good fastness. Like the previously announced members of this series, the new offerings are claimed to be particularly adapted to the production of level and speck-free prints on delustered rayon. They may also be printed on bright rayon and on acetate fiber materials with satisfactory results.

"Pontamine" Fast Black LCW—a direct dyestuff recommended by the manufacturers exclusively for dyeing cotton materials containing acetate fibers that are to be left clear. It is said to be of good application and fastness properties and is particularly recommended by the manufacturers for producing light and medium grays although it may also be used for full shades of black. Compared with the division's older type, "Pontamine" Fast Black L, the new offering is noticeably brighter and somewhat bluer in shade.

"Diagen" Red MG Concentrated Solution—a stabilized azoic printing color. It produces bright red prints said to be of satisfactory fastness. It is a stable product which it is stated has been carefully controlled to insure the best printing results, and it is easy to apply and ages rapidly. Like the rest of this class of colors, "Diagen" Red MG Concentrated Solution is principally employed on ladies' dress-goods, handkerchiefs, scarfs, and similar fabrics where brilliancy and ease of application are required.

Several vat colors manufactured in grain form have recently been placed on the market by the du Pont Company. These include:

"Ponsol" Golden Orange GS Double (Patent Applied For).

"Ponsol" Golden Orange RRTS Double (Patent Applied For).

"Ponsol" Brown AGS Double (Patent Applied For).

"Ponsol" Brown ARS Double (Patent Applied For).

"Ponsol" Khaki 2GS Double (Patent Applied For).

"Sulfanthrene" Pink FBS Double (Patent Applied For).

"Sulfanthrene" Pink FFS Double (Patent Applied For).

"Ponsol" Red G2BS Double (Patent Applied For).

"Ponsol" Violet BNXS Double (Patent Applied For).

"Ponsol" Blue BFS Double (Patented).

"Ponsol" Jade Green S Double (Patented).

"Ponsol" Olive ARS Double (Patent Applied For).

"Ponsol" Direct Black 3GS Double (Patented).

All of these products are said to be stable to storage so that there is little possibility of the formation of lumps even after a prolonged period. The new offerings are claimed to be equal in strength to the corresponding double paste brands and to possess the excellent fastness properties of the older types. The vat color grains, because of their excellent state of dispersion and fineness, are said to make it possible to obtain eminently satisfactory results in dyeing by the pigment pad and package machine methods.

"Diagen," "Acele," "Celanthrene," "Sulfanthrene," "Ponsol," and "Pontamine" are registered trade-marks of E. I. du Pont de Nemours & Co., Inc.

• CIBA RELEASES

The following new products are described in circulars issued by the Ciba Co., Inc., manufactured by Society of Chemical Industry in Basle:

Invadine B (patented)—a new wetting-out agent for use especially in cold chlorine bleach baths. The product is said to be neutral and lime-resistant and may be used in baths containing lime. Another use of this new product is in the padding of direct dyes on cotton goods which have not yet been boiled off; an addition of 10-20 gr. per liter is added to the dye solution and then the color developed later by a run through a boiling concentrated Glauber salt bath. Circular No. 443.

Cibanone Blue 2R, Micro powder for Dyeing and *Cibanone Violet 6B, Micro powder, (pat. applied for)*—two new dyestuffs, which on account of the superior fastness properties claimed for them are ranked among the best obtainable. Cibanone Blue 2R, Micro powder for Dyeing is dyed by method CI and yields a somewhat redder shade than Cibanone Blue RSN, but is said to possess a considerably better fastness to chlorine and mercerization. This product is adapted for the dyeing of cotton in all stages of manufacture, Viscose, Tubize and Bemberg in all goods requiring the highest degrees of fastness, (kier-boil and bleach). Cibanone Violet 6B, Micro powder dyes a shade considerably bluer than Cibanone Violet 2RB. The new dyestuff is said to be suited for the dyeing of all known types of rayon as well as boiled-off silk and for printing on Cotton, Silk and Rayon fabrics. It may also be used for dyeing yarns which have to be subjected to kier-boil and bleach. Circular No. 446.

Cibacete Discharge Blue 3G (pat. applied for)—a new brilliant, greenish toned blue for Acetate fiber. Heretofore it is stated it has not been possible to produce so pure a shade of blue that would still be dischargeable. Cibacete Discharge Blue 3G has, moreover, it is claimed, a very good property of levelling so that by combination with such dischargeable colors as Cibacete Yellow GN, Cibacete Orange 2R, 4R, Cibacete Scarlet G, BR and Cibacete Red GR, GGR, most of the current tones of light, medium and navy blues, greys, biege and brown, may easily be made with good dischargeability. The dyeings are said to have a good fastness to light, very good fastness to water, perspiration, acids and crocking. Cotton and Viscose are scarcely tinted; wool and silk are tinted more strongly, but may be cleared by a treatment with Hydrosulphite BZ, water soluble. Cibacete Discharge Blue 3G is

said to be well suited for the direct printing of Acetate fabrics, the prints being fast to subliming. Circular No. 448.

Chlorantine Fast Green 5GLL (patented)—a new member of the notably light-fast LL series of Chlorantine Fast Colors. This product has an especially pure clear tone and is considerably yellower than the type Chlorantine Fast Green BLL. It is particularly recommended by the manufacturer for the dyeing of cotton and viscose in skein or piece, for goods where fastness to light is the main consideration, such as draperies and upholstery goods. It is said to be particularly useful for dyeing viscose of unequal affinity in level shades. In fabrics of cotton and viscose, both fibers are dyed in a uniform shade, acetate fibers are only reserved in pale tones. Unweighted silk may be dyed in a neutral or slightly acidulated salt bath with Chlorantine Fast Green 5GLL, as well as in a broken soap bath. When dyeing half-silk in a neutral Glauber salt bath, the silk is dyed bluer and deeper than the cotton, but in an alkaline bath it remains lighter. In wool-silk mixtures, the silk dyes lighter than the wool in an acetic acid bath, but in a neutral bath the silk dyes somewhat bluer. In half-wool dyeing at a boil, the wool dyes brighter and deeper than the cotton. Chlorantine Fast Green 5GLL is not suitable for printing as an application print, nor are the dyeings on cotton or rayon dischargeable with hydrosulphites. An after-treatment with Sapamine KW slightly blues the shade, increases the fastness to water, but has no influence on the light fastness. Circular No. 450.

● JOINS WARWICK

M. M. McCann, formerly with the Burlington Mills as supervisor of research in chemical and manufacturing problems as well as being manager of dyeing and finishing, has joined the technical staff of the Warwick Chemical Co. in charge of technical service.

● REMOVE OFFICE

J. S. Young & Co. and Young Aniline Works have announced the removal of their office to 11 Park Place, New York, N. Y., as of March 28th.

● GENERAL RELEASES

General Dyestuff Corp. announces release of circulars on the following new products:

Fast Golden Orange Salt G R—which on Naphtol AS is said to produce the yellowest shades so far possible, which, it is stated, possess the very best all around fastness properties. Circular I. G. 1120.

Fast Silk Yellow G—a new acid yellow brought out by the I. G. and offered to the trade by General. It is said to draw very well from a neutral or even slightly alkaline bath and is therefore said to be especially suitable for the dyeing of tin weighted silk. It may also be used in the boil-off liquor. It is said to be of good fastness to light and washing. Circular I. G. 1156.

Soromine W F—a new softening agent brought out by the I. G. It is said to not only impart a soft handle to the rayon or cotton treated but also fills the rayon. The product may be used together with any of the auxiliaries customarily used in sizing. The stability towards Epsom salt sizes is limited, i.e., it will, for instance, flake out after some time in Epsom salt solutions of 5-175 lb. per 100 gallons, but remains dissolved in higher concentrations so that it can be used in so-called weighting finishes. The addition of Igepon T will effectively prevent a precipitation of the Epsom salt. Circular I. G. 1110.

● PERKINS CONTINUES OPERATIONS

While Holyoke and nearby towns in Massachusetts suffered severely from the flood, the plant of B. F. Perkins & Son, Inc., was able to continue operations without interruption during the high water. Manufacturing facilities were not in the least impaired by the flood. The plant, which is relatively new, was built on well-drained land above the general level which floods invade. A. C. Lade, general manager, reports that shipments are being made as usual.

● ONYX FELLOWSHIP

According to the annual report of the Mellon Institute, R. N. Wenzel, working on a fellowship of the Onyx Oil and Chemical Co. and Associated companies, has "continued during the year his investigations relating to processing compounds for textile finishing. Particular attention has been given to the improvement of preparations for the waterproofing of open fabrics. The water-repellent properties of an extensive list of available waterproofing agents have been explored by measurement of interfacial contact angles; procedures have been developed for preparing the most active agents in the form of concentrated aqueous emulsions, which were required to be fluid, stable of controlled pH, effective from extremely dilute baths, and compatible with auxiliary agents used to modify the appearance or feel of the finished fabric. This research has led to the manufacture of new products now being offered to textile mills. The fellowship has also cooperated with the donor in certain investigations pertaining to a new line of sulfonated products for use as wetting, emulsifying and levelling agents."

● L. T. I. NEW YORK ALUMNI

The regular semi-annual meeting of the New York chapter of the Lowell Textile Institute Alumni Association will be held in the Old Timers' Grill, 7 East 40th St., New York City, on Wednesday evening, April 22nd, at 6 P. M. Dr. Paul H. Nystrom, formerly of the Universities of Wisconsin and Columbia University, will speak on "Current Trends of Fashion and Retail Sales as Applied to Textiles."

● PHOTOELECTRIC REFLECTOMETER

A new photoelectric reflectometer said to measure the *reflectance, opacity* and *color* of paints, papers, pigments, powders, ceramic products, textiles and chemicals has been placed on the market by the Henry A. Gardner Laboratory, Inc., 2201 New York Ave., N. W., Washington, D. C. This new reflectometer is a photoelectric adaptation of the Hunter Visual Reflectometer first described in 1934. The photoelectric instrument measures the same quantities, employs the same large sample areas, and is said to operate much faster and with higher precision than the former visual instrument.

● TEXTILE FOUNDATION REPORT

E. T. Pickard, secretary of the Textile Foundation, makes known that a description of reports made by research fellows of the foundation has been prepared in pamphlet form and is now available to anyone making a written request for it. The reports are usually written in scientific and technical language and are of particular interest for study by technical men.

Requests for copies of the pamphlet should be addressed to the Textile Foundation, Commerce Building, Washington, D. C.

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WANTED—Textile chemist, experienced in cotton printing for demonstrating and laboratory research. Write Box No. 896, American Dyestuff Reporter.